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THE UNIVERSITY OF ALBERTA

ENTHALPY OF SOLUTION OF CO_2 AND H_2S IN DIETHANOLAMINE SOLUTIONS

by

AZAMUL KAHRIM

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

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DEPARTMENT OF CHEMICAL ENGINEERING

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled "ENTHALPY OF SOLUTION OF CO_2 AND H_2S IN DIETHANOLAMINE SOLUTIONS", submitted by Azamul Kahrim in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

A E Mather
Supervisor

Loren Hepler

J. A. Ollis

Date 14th April 1976

TO MY MOTHER

ABSTRACT

An adiabatic calorimeter was designed, constructed and used to measure the differential heat of solution (ΔH_s) of CO_2 and H_2S in aqueous diethanolamine (DEA) solutions.

Experiments were performed to apply the method[19,27] of comparative measurements, and the method[4] of slope was used to determine the heat of solution. As heat capacity data were needed to reduce the measured quantities into the heat of solution data, heat capacities were measured for both the fresh and loaded amine solutions. As well densities were measured for both the fresh and loaded amine solutions. An enthalpy-concentration diagram was constructed for one of the CO_2-DEA systems. Measurements were made over the range of normalities from 2.0 N to 5.0 N and over the range of temperatures from 25°C to 75°C.

The differential heat of solution of CO_2 in 2.0 N, 3.5 N, and 5.0 N DEA solutions was measured at 25°C. At 50°C measurements were made with 2.0 N and 3.5 N DEA solutions, and and at 75°C only one normality, 3.5 N, was investigated.

At 25°C, the differential heat of solution of CO_2 in DEA was found to be independent of 1) amine concentration, and 2) solution loading α. At 50°C and 75°C the differential heat of solution decreased with increasing α, and was dependent on the solution strength (N). As the temperature increased (from 25°C to 75°C), ΔH_s was found to be a stronger function of temperature than normality.

The differential heat of solution of H_2S was measured for one normality, 3.5 N and one temperature, 25°C. ΔH_s increased slightly with increasing concentration of H_2S in solution. The heat capacity data for this case were collected but no density measurements were made.

Prior to this work no heat capacity or density data were available for DEA solutions containing dissolved CO_2 or H_2S. The differential heat of solution data available in the literature[16,18,21] were obtained by differentiation of the partial pressure solubility data. The calculated ΔH_s values obtained from the literature were compared with the experimental results of this work. The comparisons were not exact, because of the non-uniformity of conditions such as normalities and temperatures for the calculated and experimental data. The calculated data of Lee, Otto and Mather[16,18] agreed best with the experimental results of this work.

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NOMENCLATURE

a, b	Liquid sample mass
A, B	Area
B, C, D	Coefficients in Equation (80)
C_1, C_2	Corrections in Equation (33)
Cp	Constant pressure heat capacity
E	Potential Difference
g	Rate of change of temperature
h	Specific enthalpy
H	Enthalpy
I	Current
k	Thermal leakage modulus
K_a	Equilibrium constant
m, n	Quantities of each component
N	Normality
p	Thermal powers
P	Pressure
Q	Energy
R	Gas Constant
t	Time
T	Temperature
u	Quantity in Equation (3)
V	Voltage
x	Mole fraction
α	Mole ratio
ϵ	Energy equivalent

δ	Small difference
Δ	Difference
ρ	Density

Subscripts

b	Start of main period
c	Chemical measurement
corr	Corrected
cum	Cumulative quantity
e	End of main period
e	Electrical measurement
f	Final
i	Initial
j	Jacket
s	Solution
t	Total
xa, xb	Points at which areas A and B are equal
1, 2	Components 1 and 2
1, 2, 3	States 1, 2 and 3
αi	A solution loading αi
∞	Infinity

Superscripts

*	Linearized property
**	Linearized and corrected
'	At temperature of state 1
"	At temperature of state 2

INTRODUCTION

The alkanolamines are the most generally accepted and widely used of the many available solvents for removal of CO_2 and H_2S from gaseous hydrocarbon streams. Basically the process involves first the removal of the acid gas in an absorber column and the regeneration of the solvent in a stripper column. In the absorption process heat is released, and in the stripping operation energy is required to separate the acid gas from the solvent which is then recycled to the absorber.

To date, gas sweetening plants have been over-designed because of the lack of fundamental data on the thermal aspects of the process. This results in the excessive consumption of both material and energy. Our current awareness of the exhaustibility of our conventional energy supplies, necessitates that the engineer design from a socioeconomic standpoint, more so than ever before.

This project was undertaken to obtain data which would aid in the design of more efficient and economical gas sweetening processes, using diethanolamine as the solvent. In the process, savings can be achieved by reducing the solvent circulation rate, and through utilization of the energy stored in the loaded amine solution leaving the absorber. Since the circulation rate is set by an energy balance around the absorber, accurate heat of solution and heat capacity data are required to calculate the optimum circulation rate.

The data to be measured consisted of heat of solution data, heat capacity data and to a lesser extent density data for the CO_2-DEA and H_2S-DEA systems. To be of practical importance, the differential heat of solution was determined; conventionally, most heat of solution data have been reported at infinite dilution.

In Chapter I the scope of the work and the functional requirements of the equipment to be used are discussed. Chapter II covers the design and construction of the equipment, and the experimental procedures used in obtaining the data. Because of the variety of data being determined, a fair amount of computations was needed to present the data in a usable form; the major steps used to reduce the raw data to a usable form are explained in Chapter III. Finally, in Chapter IV the experimental results are presented and compared with the calculated heat of solution values used in the design of gas sweetening plants in operation today.

CHAPTER I

PRELIMINARY CONSIDERATIONS

In this chapter a general discussion on calorimeters is presented. The two types of calorimeters seriously considered for this work are described from the point of view of the applicability of each type. Finally, the special design considerations that the chosen calorimeter must possess, are outlined.

A. Calorimeters

Calorimeters have been used to measure thermal properties of materials for close to a century. A calorimeter is accepted today to mean an instrument to measure the heat evolved or absorbed in a known change in state of a material. This can involve a change in phase, temperature, pressure, volume, chemical composition, or any other property of the material which is associated with a change in energy. A calorimeter can measure the energy involved either directly by comparison with a known electrical energy or indirectly by comparison with materials with known properties. The many methods of calorimetry along with the details of the respective calorimeters have been compiled into a textbook by McCullough and Scott.[19]

Of particular interest in this work were isothermal and adiabatic calorimeters. Isothermal calorimeters, as the name implies, are those in which there is ideally no change in temperature during the experiment. An adiabatic calori-

meter is one which ideally has no heat transfer across the boundaries. The two specific types of calorimeters considered for the measurement of the heat of solution were 1) Bunsen calorimeters and 2) Dewar type calorimeters.

1) Bunsen Calorimeters

Bunsen calorimeters are isothermal calorimeters, in which the heat involved in a process is measured indirectly by utilizing known properties of other materials. The earliest variety were Bunsen ice calorimeters. These utilized the change in volume associated with the ice-water phase change as a measure of the heat involved in a process.

A Bunsen ice calorimeter is basically two concentric cylindrical type vessels, immersed in an ice bath. The outer vessel is transparent, and the inner vessel in which the heat change takes place, is made from a good heat-conducting material. An ice mantle is deposited on the outer surface of the inner vessel. The ice condition is monitored by visual inspection through the outer vessel. Usually, some material less volatile than water, mercury for instance, is connected to the ice-water chamber to monitor the change in volume as the ice changes into water or vice-versa. Opdycke et al.[23] described the construction and operation of an ice calorimeter.

In more recent times, diphenyl-ether has replaced ice as the material used in forming the mantle. Davies and Pritchard[6] described in great detail the construction and properties of a diphenyl-ether calorimeter used in measuring

the heat of solution of hydrogen chloride gas in water. The major advantages of diphenyl-ether over ice are 1) the proximity of its melting temperature (26.9°C) to the standard reference temperature of 25°C, and 2) the volume change on melting is about three times as great. Bunsen type calorimeters have played a significant role in the field of calorimetry but for the task at hand there were some limitations with this type of calorimeter.

The major limitation, which is inherent to the calorimeter, is the fact that measurements can only be made at one temperature, the melting temperature of the mantle. The ultimate goal of this study was to measure the heat of solution of CO_2 and H_2S in aqueous amine solutions, under conditions which were similar to those encountered in industry. One such condition is a range of temperatures extending to 100°C. Other disadvantages associated with the calorimeter are the long times involved in preparing the mantles and the rigorous measures needed to maintain them. More generally, the extremely delicate nature of the calorimeters (which must be constructed from glass) was also a deterring factor. For these reasons it was necessary to look at other types of calorimeters.

2) Dewar Type Calorimeters

The basic principle of this calorimeter design have been thoroughly covered by Sturtevant[28] and Rossini[27] and numerous references to specific designs are given in these sources. Consistent with these principles the calorimeter

vessel is basically a one litre silvered Dewar. A metal lid fitted with several ports is clamped onto the top of the Dewar. The ports are used to house 1) temperature measuring devices, 2) a mechanical stirrer, 3) a heater, and one port serves as the entrance into the calorimeter vessel. The entire system is immersed in a thermostated bath.

Operation:

This type of calorimeter utilizes the method of comparative measurements to determine the enthalpy change in the process under investigation. If the process under study is exothermic, the experiment is performed inside the Dewar and the temperature rise detected. An electrical calibration is done next and the temperature rise recorded. After applying several corrections, mainly for heat leakage, the heat released in the reaction is determined by comparing the two increases in temperature, and by evaluations based on the known amount of electrical energy supplied.

This calorimeter could be operated in two modes.

a) The bath temperature could be controlled to be the same as the calorimeter temperature at any point in time. By minimizing the temperature difference between calorimeter and surroundings the calorimeter is made more adiabatic through reduction of the heat exchange between the calorimeter and surroundings.

b) The bath temperature could be kept constant while the temperature in the calorimeter increases. The term isoperibol[19] has been suggested to describe this mode of

operation. More heat exchange takes place in this mode as compared to (a), and larger corrections are needed, but the actual operation is simpler.

Isoperiol calorimeters of the same basic design have been used by Vanderzee and Nutter[32], Vanderzee and Rodenburg[33], and Vanderzee and Gier[30], to measure the heat of solution of gaseous hydrogen chloride, hydrogen fluoride and hydrogen iodide in water, at 25°C. In a survey of the literature, the work of Vanderzee and co-workers was the only material found bearing a resemblance to the work envisioned here. The significant difference between all work in the literature, and this work as planned, was the fact that the heats of solution reported in the literature were always done at infinite dilution. In other words a small amount of solute (e.g. HCl) was dissolved in a large amount of solvent (water).

The differential heat of solution is a function of composition, and for this reason data are reported at infinite dilution. One of the prime objectives of this study was to measure the differential heat of solution. That is, the heat of solution of CO_2 and H_2S in diethanolamine solutions, as a function of increasing acid gas content in solution. With this in mind, several changes are needed to adopt the basic Dewar-type calorimeter to measure the heat of solution of CO_2 and H_2S in DEA solutions.

B. Design Considerations For Isoperibol Calorimeter

The Dewar-type calorimeter operating in an isoperibol mode was chosen for this work. Referring back to the work of Vanderzee and co-workers, in measuring the heat of solution of the gaseous halogen acids at infinite dilution, "one-shot" measurements were done. The quantity of solute required to cause about a 0.5°C rise in temperature was predetermined and then used in the actual experiment. The increase in temperature was deliberately kept to a maximum of 0.5°C to reduce heat losses to the surroundings.

In this work the gaseous CO_2 and H_2S are to be dissolved incrementally, and the heat of solution determined after each dissolution, until the solution is saturated at atmospheric pressure. In this way the heat of solution can be reported as a function of increasing composition of acid gas in solution.

Prior to the actual experiments, pilot runs indicated that a temperature rise of 0.5°C was not practical for this work. A temperature rise of approximately 3°C was adopted. With the quantity of gas causing the 3°C temperature rise, saturation can be achieved after 8 to 10 incremental dissolutions for either CO_2 or H_2S. Heat exchange would be larger compared to the work of Vanderzee and others, but the appropriate corrections would have to be applied as explained in Chapter III.

Other design features decided on for the calorimeter are as follows:

1) the construction material must be inert to resist corrosion caused by H_2S and diethanolamine. Stainless steel was chosen.
2) temperature measurement would be performed in the differential mode to improve accuracy. The constant temperature bath, in which the calorimeter was immersed would serve as a reference.
3) the stirrer used should be the magnetic coupling type to avoid the placement of a stirring shaft through the lid of the calorimeter. By not placing a stirring shaft through the lid, the possibility of oil seepage into the calorimeter and gas leakage out of the calorimeter would be reduced.

And finally,

4) consistent with the above mentioned features the calorimeter would operate in an isoperibol mode.

CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus used in this work is described in Section A of this chapter. Section B covers the experimental procedures used in performing the measurements.

A. Description of the Apparatus

The apparatus consisted of four main components, namely,

(1) a calorimeter and lid,

(2) a magnetic stirrer,

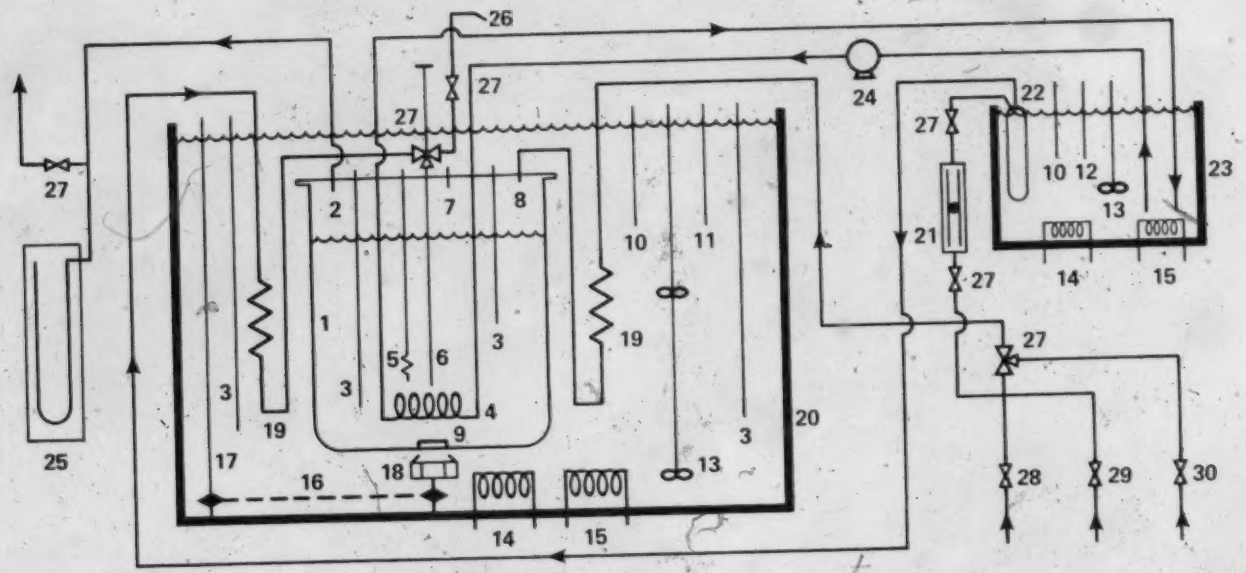
(3) a constant temperature oil bath, and

(4) a cooling water bath

A schematic flow diagram of the apparatus is shown in Figure 1. The details of the construction are as follows:

1. Calorimeter and Lid

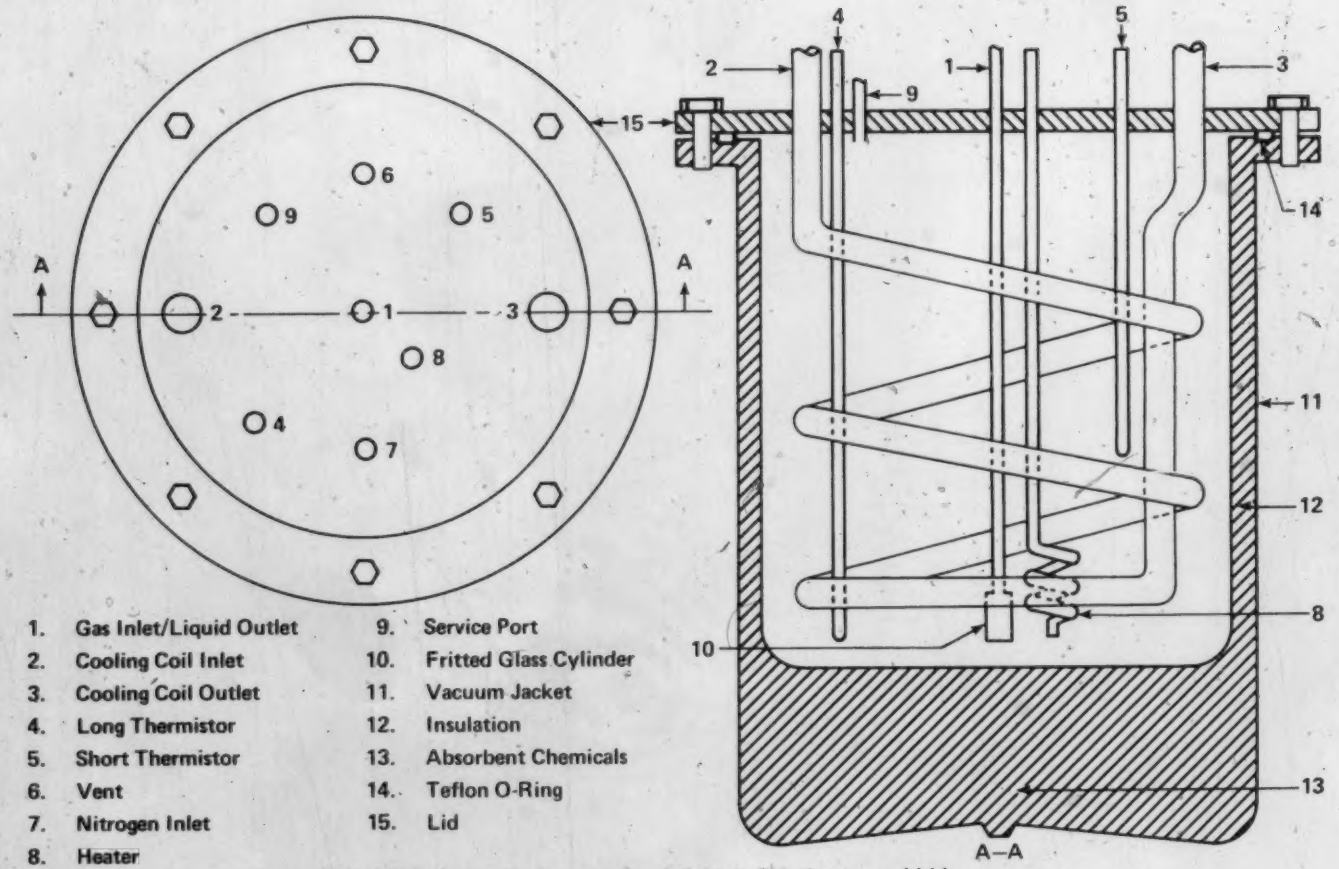
A detailed drawing of the calorimeter and its lid appears in Figure 2. The calorimeter was obtained from Andonian Cryogenics Inc. and it was basically a 1.5 litre stainless steel Dewar fitted at the top with a flange carrying a groove for an O-ring seal against which the lid was clamped. The inner and outer diameters of the calorimeter were 4.5 and 5.6 inches and the inner and outer depths were 6.0 and 8.6 inches respectively. The calorimeter featured a double wall separated by a vacuum of 0.7 mPa or better between the walls. At the base, between the walls there was a spun copper chemical holder containing an adsorbent chemical. The calori-



LEGEND

1. Adiabatic Calorimeter
2. Calorimeter Vent
3. Thermistors
4. Cooling Coil
5. Calorimeter Heater
6. Gas Inlet/Liquid Outlet
7. Service Port
8. N_2 Inlet
9. Magnetic Stirring Bar
10. Sensor For Heat Input Controller
11. Platinum Thermometer
12. Mercury Thermometer
13. Bath Stirrer
14. Controlled Heat Input
15. Cooling For Bath
16. Gear Train For Magnetic Stirrer
17. Shaft For Magnetic Stirrer
18. Turning Magnet
19. Inlet Tubing For Calorimeter
20. Oil Bath For Calorimeter
21. Rotameter
22. Presaturator
23. Bath For Calorimeter Cooling Water
24. Pump
25. Manometer
26. Liquid Sampling Port
27. Flow Regulating Valves
28. Shut-Off Valve For CO_2
29. Shut-Off Valve For H_2S
30. Shut-Off Valve For N_2

FIGURE 1. Schematic Flow Diagram of Apparatus



1. Gas Inlet/Liquid Outlet
2. Cooling Coil Inlet
3. Cooling Coil Outlet
4. Long Thermistor
5. Short Thermistor
6. Vent
7. Nitrogen Inlet
8. Heater
9. Service Port
10. Fritted Glass Cylinder
11. Vacuum Jacket
12. Insulation
13. Absorbent Chemicals
14. Teflon O-Ring
15. Lid

FIGURE 2. Assembly Drawing for Adiabatic Calorimeter and Lid

meter was not recommended for any pressures greater than 70 kPa.

The lid of the calorimeter was fabricated from stainless steel 0.5 inch in thickness and there were nine ports in the lid. The function of each port was as follows.

a) Port 1 served a dual purpose for gas entry and liquid sample removal. A piece of 1/8 inch O.D. stainless steel tubing approximately 4 inches in length extended from the top of the lid into the calorimeter through port 1. A 70-100 micron fritted glass cylinder was connected to the end of the tubing (in the calorimeter) with a short length of Tygon tubing. Stainless steel fritted cylinders of the same porosity were not used because the glass cylinders gave a much finer dispersion of gas bubbles. Also the fritted glass cylinder was not joined to the stainless steel tubing with Kovar because Kovar is known to corrode in amine solutions containing acid gases. The other end of the tubing was connected to a three-way stainless steel ball valve which was mounted on the lid. This valve directed the flow of gas in, or liquid out of the calorimeter.

b) Ports 2 and 3 were the inlet and outlet for the calorimeter cooling coil. The cooling coil was constructed from 1/4 inch O.D. stainless steel tubing and consisted of four equally spaced turns approximately 4 inches in diameter.

c) Two Conax TH 14 thermistors connected in parallel and housed in 1/8 inch O.D. stainless steel casing were mounted in ports 4 and 5. The sensing elements of the two

thermistors were not located diametrically opposite to each other; one was placed 1-1/2 inches and the other 1 inch (along the diameter) from the centre of the lid respectively. The former extended to a depth of 5-1/2 inches and the latter 4 inches from the bottom of the lid into the calorimeter. The two thermistors were used in this configuration to detect the average temperature of the calorimeter contents. Electrical details concerning the thermistors are presented later on in this chapter.

d) Stainless steel tubing of 1/8 inch O.D. and extending 1/2 inch into the calorimeter was connected to ports 6 and 7. Port 6 was the vent line from the calorimeter, and nitrogen used in forcing liquid samples out of the calorimeter entered through port 7.

e) The calorimeter heater was brought out from the lid through port 8. The heating element consisted of nine feet (240 ohms) of enameled and fibre-glass-insulated Electroloy wire (No. 36 B & S) obtained from the Molecu Wire Corp. The heating wire was tightly wound as a single layer on one end of a 3 foot length of enameled copper wire (No. 19 B & S) which served both as a support and a lead wire; when wound the heating wire formed a coil approximately 11 inches long. At the end of the coil the heating wire and the copper support were soldered and a length of insulated copper wire was soldered to the other end of the coil to form the other lead wire.

The heating coil was then covered with a silicone heat sink compound and inserted into a 2 foot length of 1/8 inch O.D. stainless steel tubing welded shut at one end. The eleven inch section of the tubing containing the coil (at the closed end) was then wound into 4 equally spaced turns 3/4 inch in diameter to form a spiral 1-1/2 inches long. The remainder of the tubing was sufficient to bring the lead wires out of the calorimeter and out of the oil bath.

In the earlier stages of this work the heater was built by winding the heating wire onto a Micarta (plastic impregnated fabric) cylindrical shell 1 inch long by 1/2 inch outside diameter. The composite shell was then covered with Devcon-F epoxy and joined with the epoxy to a length of 1/8 inch O.D. stainless steel tubing, through which the lead wires were brought out of the calorimeter. The amine solutions corroded the epoxy and eventually broke the heating wire. This design was abandoned after two attempts.

f) Port 9 is a service port used for filling, discharging and cleaning the calorimeter and it is sealed when it is not used for these purposes.

When the lid is clamped on the calorimeter, the fritted glass cylinder, the cooling coil and the heater are approximately one inch from the bottom of the calorimeter. The lid was attached to the calorimeter with a Teflon O-ring and 8 steel bolts.

2. Magnetic Stirrer

As already mentioned the stirrer to be used was to be magnetic and capable of operating while immersed in the oil bath. Therefore the design used was mechanical in nature and employed a gear-train to rotate the turning magnet. The turning magnet was made up of three rectangular magnets housed in a cylindrical aluminum block. Two flat pieces of mild steel were placed at the poles of the composite magnet (in the block) to concentrate the magnetic poles around the tips of the steel plates. The shaft of the aluminum block and the shaft for the stirring motor were anchored on a steel base made in the form of a cross. Also anchored to the cross was a cylindrical steel shell for positioning the calorimeter above the turning magnet. The design was such that the calorimeter could be removed by simply lifting it out of the shell. In composite form the calorimeter, the shell, the turning magnet and the base were essentially one unit, which was completely immersed in the oil bath.

The stirring motor shaft was connected to a 1/15 HP speed controlled motor with a flexible coupling. The magnetic stirring bar used inside the calorimeter was 1.5 inches long and a stirring speed of approximately 300 RPM was found to be adequate.

3. Constant Temperature Oil Bath

It is necessary to maintain a constant temperature around the calorimeter and its lid during the experiment.

To do this a bath first used by Lee[15] was employed in this work. The bath was a Dewar made from stainless steel and insulated with styrofoam. The net capacity was about 67 litres and the fluid used was SAE-10 motor (mineral) oil. The original 50 foot long copper coils in the bath used by Lee were replaced with soft aluminum coils of the same length because of the corrosive nature of CO_2 and H_2S. Before entering the calorimeter the feed gas (CO_2 or H_2S) was circulated through one of these coils (the same coil for either gas) to equilibrate the temperature of the gas with that of the bath. The other coil served the same purpose for N_2 whenever N_2 was used to force a liquid sample out of the calorimeter.

The original cooling coil and heaters of either 300 or 500 watts capacity were left intact in the bath. The bath was stirred by a two stage impeller driven by a 1/15 HP electric motor, and the temperature was controlled within $\pm$ 0.01°C by a Hallikainen Thermotrol temperature controller, model 1050. Dipping into the bath was a platinum resistance thermometer used in measuring the absolute temperature of the bath, and two Conax TH 14 thermistors (the same as those used in the calorimeter) connected in parallel, and positioned on opposite sides of the calorimeter. The electrical network for the thermistors is shown in Figure 3.

4. Cooling Water Bath

At the end of a measurement after the temperature of the solution in the calorimeter had increased and the

final period recorded, the solution had to be cooled to the bath temperature for the next measurement. For a difference of about 5 °C between the calorimeter contents and the bath, it would take more than a day for the system to equilibrate to the bath temperature if the calorimeter were left to lose heat to the bath by natural processes. The cooling water bath provided water to cool the solution in the calorimeter down to the bath temperature.

The bath was simply a container of 60 litres capacity filled with distilled water and equipped with the necessary instruments to maintain a set temperature. The cooling water was kept 1 to 2°C lower than the bath temperature to avoid over-cooling of the calorimeter contents. The water was pumped through the cooling coil in the calorimeter by a Cole-Parmer Master Flex pump, model 7018.

A presaturator used in saturating the feed gas was also immersed in the water bath. Not all the gas fed to the calorimeter reacted and in fact a fair amount of gas was vented as the solution in the calorimeter became saturated. In order to prevent loss of heat by evaporation caused by the portion of the gas flowing through (and not reacting), the feed gas had to be saturated before entering the calorimeter. The saturator consisted of a 150 ml stainless steel bottle half filled with an amine solution which was saturated with the acid gas under investigation, but was of the same normality as the solution in the calorimeter. By keeping the saturating solution at approximately the same temperature as

the solution in the calorimeter heat losses by evaporation were virtually eliminated.

The presaturation of the feed also prevented an increase in the normality of the solution which would have resulted from the loss of water. In fact with presaturation of the feed gas, the normality of the solution would be expected to decrease because of the addition of some water to the solution. The normality was checked throughout the experiment and it did decrease, but the change was negligible.

5. Measuring Instruments

1. The temperature of the oil bath was determined with a Leeds and Northrup platinum resistance thermometer, model number 8163. It was calibrated for use in the range 90.188 K to 773.14 K on the International practical temperature scale of 1968 by the National Research Council of Canada. The circuit diagram for the thermometer is shown in Figure 4 and the calibration data are presented in Appendix 1.

2. The difference in temperature between the calorimeter contents and the bath was detected by a set of four Conax TH 14 thermistors connected in a differential mode. Figure 3 shows the bridge network for the thermistors. The detected temperature difference was recorded by Hewlett-Packard strip chart recorder model 7100B. The calibration data for the thermistors appear in Appendix 1.

3. The electrical energy for the calorimeter heater was supplied by a Kepco DC power supply. The energy supplied was

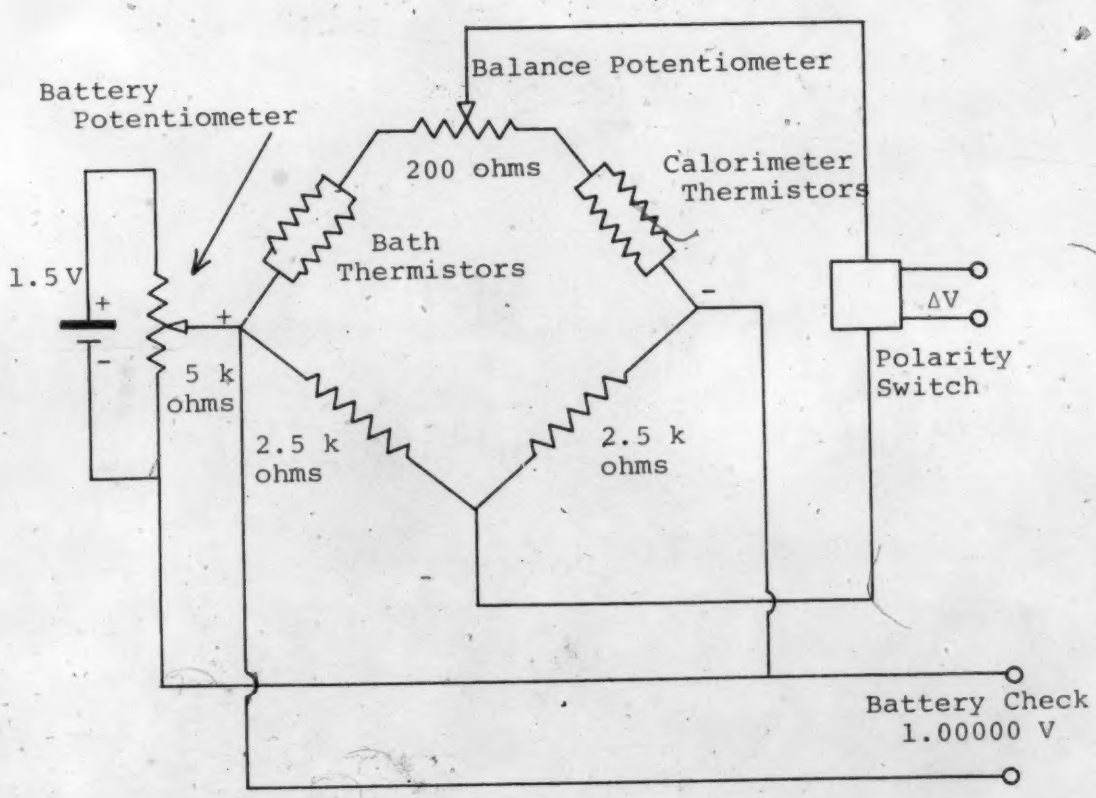


FIGURE 3. Wiring Diagram of Bridge Network for The Thermistors.

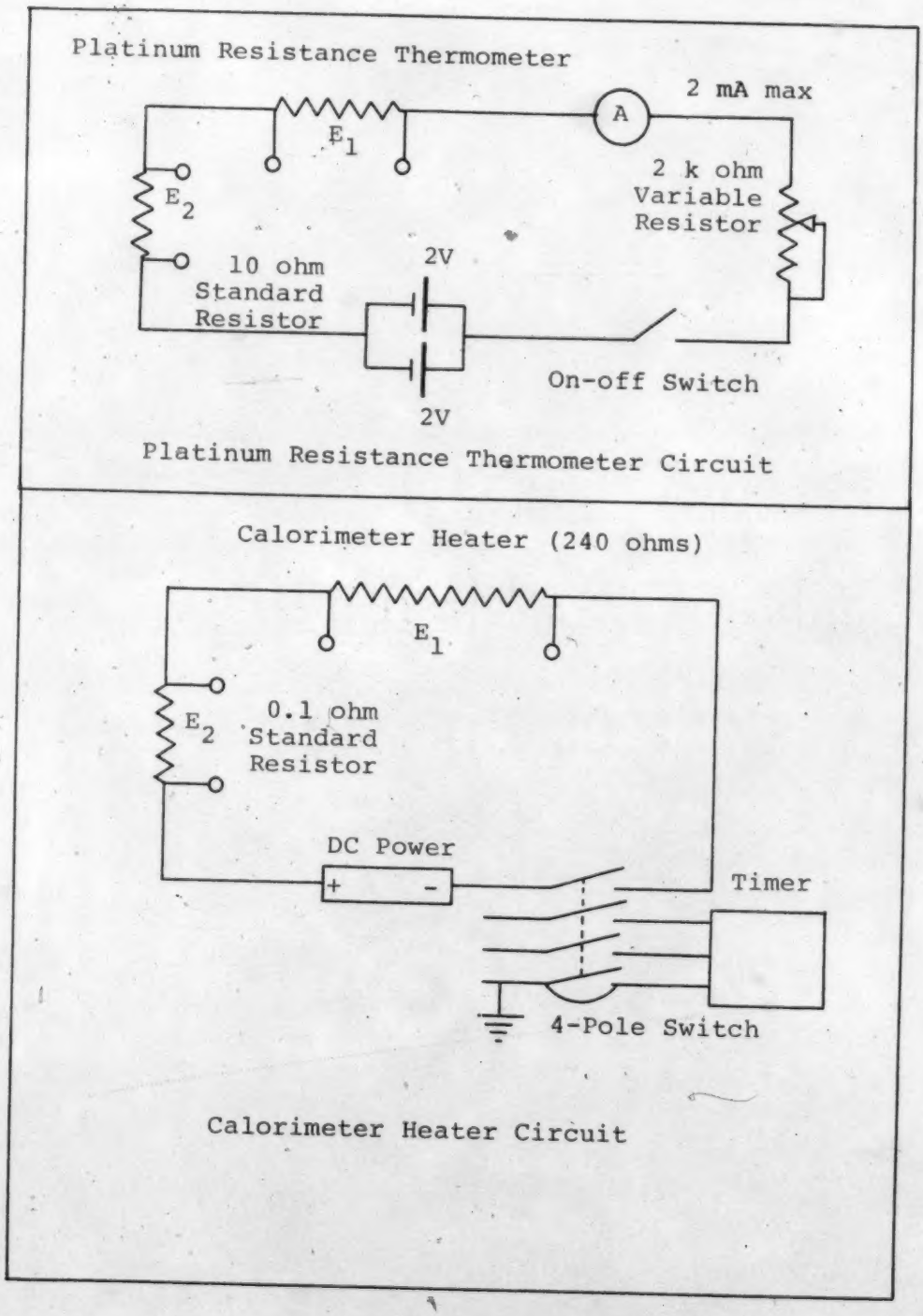


FIGURE 4. Wiring Diagrams of Platinum Resistance Thermometer and Calorimeter Heater Circuits.

measured by a timer accurate to 0.1 sec, in conjunction with a Hewlett-Packard model 3450 multi-function meter with a six-digit display. Figure 4 shows the circuit diagram for the calorimeter heater, and as shown the circuit was designed to activate the timer the instant power was supplied to the heater.

4. A thermocouple vacuum gauge was used to read the vacuum in the stainless steel Dewar (oil bath). The vacuum was less than 5 microns.

5. A mercury manometer was used to monitor the pressure in the calorimeter.

6. For indication and approximate measurement of gas flow rate to the calorimeter, a rotameter was used before the gas entered the presaturator.

By means of a multi-selection switch the following signals could be displayed on the Hewlett-Packard multi-function meter:

i) the voltage drop across the 10 ohm standard resistor,

ii) the voltage drop across the platinum resistance thermometer,

iii) the difference in voltage between the bath and calorimeter thermistors (at the same time it was being recorded on the recorder),

iv) the voltage drop across the 0.1 ohm standard resistor,

v) the voltage drop across the calorimeter heater and,

vi) the battery check in the thermistor bridge which was maintained at 1.00000 ± 0.00015V by adjustment of the battery potentiometer.

6. Flow Pattern

Figure 1 also shows the paths taken by N_2, CO_2 and H_2S through the system. A cross connection permitted the flow of CO_2, H_2S or N_2 through the fritted glass cylinder into the calorimeter. The N_2 supply was connected to the cross for safety reasons.

At the completion of an experiment with H_2S, the H_2S was desorbed from solution by bubbling N_2 through the solution, before removing the solution from the calorimeter. N_2 used in the back forcing of a liquid sample out of the calorimeter entered from the top of the calorimeter.

B. Experimental Procedures

1. Start-Up

One litre of the amine solution at room temperature was weighed and then charged to the calorimeter. At this time all valves were placed in the closed position. The bath stirrer and the Thermotrol were then turned on. Approximate Thermotrol settings for each desired temperature were available from the operating manual of the Thermotrol. Once the temperature of the bath had increased to around the desired value the coolant to the bath was turned on. By fine tuning the Thermotrol controls and the flow rate of the coolant,

equilibrium at the desired temperature was reached within a period of 3 to 4 hours. Ethylene glycol kept at 18 to 19°C was used as the coolant for a bath temperature of 25°C and the cold water supply served as the coolant for 50°C and 75°C respectively.

After the bath reached equilibrium the calorimeter stirrer, the thermistors and the strip chart recorder were turned on. The proper scales and speeds for the recorder were of utmost importance in this work. Ultimately, the "corrected temperature rise" of the calorimeter contents over the bath have to be evaluated from the recorder chart. The technique used for evaluation of the temperature rise was a modified[12] version of the Dickinson[7] extrapolation method and its development is presented in Chapter III. The scales used on the recorder in this work were 50 mV full scale for bath temperatures of 25°C and 50°C and 20 mV full scale for 75°C. These scales were dictated by the bridge network for the thermistors and the value of the temperature difference to be measured. The chart speed was fixed at 0.2 inches per minute for all bath temperatures. This speed produced time-temperature curves which were suitable for applying the Dickinson extrapolation method.

The contents of the calorimeter were usually cooler than the bath. With the voltage supply set at approximately 100V the calorimeter heater was turned on until the calorimeter and bath temperatures were about the same. The entire

system was then left to come to thermal equilibrium, which took 1/2 to 1 hour.

Once the system reached equilibrium an electrical measurement was made to determine the heat capacity of the unloaded amine solution. Matched pairs of chemical and electrical measurements were then made to determine how the heat of solution and also the heat capacity of the loaded solution depended on the solution loading, α. These pairs of measurements were continued until the acid gas would no longer dissolve at atmospheric pressure. The procedures used to perform the electrical and chemical measurements are presented next.

2. Electrical Measurements

To determine the heat capacity of the unloaded amine solution the energy required to increase the temperature of the solution by approximately 3°C in a time interval of 3 to 4 minutes was supplied from the calorimeter heater. During the main period when the heater was on, the voltage drops across the 0.1 ohm standard resistor and the calorimeter heater were recorded after every 30 seconds. After about every 1°C rise in temperature the battery voltage in the thermistor bridge was checked and restored to 1.00000 $\pm$ 0.00015V by adjusting the battery potentiometer. After the heater was turned off the total time clocked by the timer was noted. At this point the time-temperature curve changed from being a record of the main period into a record

of the final period and took on a negative slope. The final period was recorded for 25 to 30 minutes.

The solution was then cooled to the bath temperature by pumping cooling water through the cooling coil and at the same time the battery voltage was restored to 1.00000 ± 0.00015V. The calorimeter and contents was left for 1/2 to 1 hour to come to equilibrium before the next measurement was made.

The next measurement made was a chemical measurement (as described later on in this chapter) and then the electrical equivalent. The objective in each equivalent electrical measurement was to duplicate the main period of the time-temperature curve of the previous chemical measurement. In other words an equal temperature increment in the same time period must be reproduced by supplying heat to the solution via the calorimeter heater. Independently, the temperature rise could be achieved with many different values of the voltage drop across the heater, but simultaneously with the time constraint, the voltage across the heater had to be controlled. This was done by utilizing the conditions of the previous electrical measurement.

Two assumptions were made, 1) the heat capacity of the solution did not change significantly, and 2) the mass of the solution remained almost constant since the previous electrical measurement. It can be shown that if a voltage drop $V_{e,1}$ across the heater produced a temperature rise of

ΔT_e in a time t_e, the voltage drop $V_{e,2}$ required to produce an increase of ΔT_c in time t_c is :

$$V_{e,2} = V_{e,1}\sqrt{\frac{\Delta T_c \times t_e}{\Delta T_e \times t_c}} \qquad (1)$$

In this illustration subscripts e and e,1 refer to the previous electrical measurement made and subscript c refers to the chemical measurement to be duplicated.

Therefore before doing the equivalent electrical measurements the voltage was preset on the power supply before the heater was turned on. With this approximate setting it was possible to duplicate the temperature rise and time span within 5% or less of those encountered in the main period of the chemical run in question. Once the heater was switched on, the same procedure described above was used in recording the main and final periods of the equivalent electrical measurement. At the end of each electrical measurement, after the solution was cooled to the bath temperature, a liquid sample was removed using the method described later on in this chapter.

3. Chemical Measurements

The first chemical measurement was done after the heat capacity of the unloaded amine solution was determined. To perform a chemical measurement the flow path of the CO_2 or H_2S was opened in the following order:

1) the shut-off valve for the gas supply was opened and the delivery pressure set at 40 psig,
2) the valve on the vent line was opened,
3) the three-way ball valve on the lid of the calorimeter was positioned for gas flow into the calorimeter and,
4) the valve between the rotameter and the presaturator was opened last.

The multi-function meter was positioned to monitor the battery voltage. Gas flow to the calorimeter commenced by opening the metering valve of the rotameter. At the same time a separate timer was started manually to record the duration of gas flow to the calorimeter. As the temperature increased in the calorimeter the battery voltage was restored to 1.00000 $\pm$ 0.00015V. To terminate the flow of gas after the temperature of the solution had increased by approximately 3°C the following procedure was used:

1) the three-way ball valve was placed in the closed position and at the same time the manual timer was stopped,
2) the metering valve of the rotameter was closed and finally,
3) the valve between the presaturator and the rotameter was closed and the time clocked by the timer was noted.

This sequence was used to avoid the back forcing of liquid

from the calorimeter into the gas coil, as a result of pressure build-up in the calorimeter. Some of the scatter in the heat capacity data collected in the early stages of this work (i.e. 25°C) was due to small amounts of liquid being forced into the gas coil.

The duration of the final period for the chemical measurements was not the same as it was for the electrical measurements (25 to 30 minutes). The shape of the time-temperature curve for the final period changed from chemical measurement 1 to chemical measurement 2 etc., as the solution became increasingly saturated. For low values of α, approximately 0 to 0.3 for CO_2 and 0 to 0.4 for H_2S, the temperature of the solution increased slowly as the small quantity of gas above the solution in the calorimeter continued to react, even though the gas flow to the calorimeter had stopped. On completion of the reaction the time-temperature curve conformed to those seen in the electrical measurements.

With higher values of α the solubility of the gas in the solution progressively decreased. Eventually the time-temperature curve took on a negative slope soon after the gas flow was stopped. The criterion used in determining how long the time-temperature curve should be recorded was a time of 25 to 30 minutes after the curve had achieved a negative slope. The solution was then cooled and the battery voltage restored to 1.00000 $\pm$ 0.00015V. The system was then left to come to equilibrium for a period of 1/2 to

1 hour before the equivalent electrical run was made.

As the solution became saturated minor changes had to be implemented to achieve the 3°C temperature rise in an acceptable length of time. For CO_2 the flow rate was increased from 1.6 to 2.0 litres/minute from the first to the last chemical measurement. As the flow rate increased a larger portion of the gas flowed through the solution and out the vent without reacting. With this increase in flow rate about 70% of the chemical measurements were made with the 3°C temperature rise occurring in 3 to 5 minutes. At the upper limit of 2.0 litres/minute the time needed approached 11 minutes. At this point the solution was saturated at atmospheric pressure and any attempt to further dissolve gas resulted in the gas desorbing immediately after the gas flow was terminated. Desorption was monitored by closing the vent valve and observing the manometer. In fact, this check was performed after every chemical measurement by closing the vent valve for a few minutes during the final period.

For H_2S the flow rate was increased from 1.6 to 2.2 litres/minute and about 75% of the measurements were made with the 3°C temperature rise occurring within 3 to 5 minutes.

This behavior was observed for the three bath temperatures, namely, 25°C, 50°C and 75°C.

While monitoring for desorption (after every chemical measurement) an unexpected occurrence was noticed.

For a small percentage of the chemical measurements the residual gas in the calorimeter continued to react after the time-temperature curve had achieved a negative slope. This was substantiated by the gradual decrease in pressure in the calorimeter, as indicated by the manometer. With these cases it was not practical to wait for the last trace of gas to react, so the reaction was quenched just before cooling (i.e. after the 25-30 minutes observation period). N_2 was flowed above the liquid in the calorimeter for 10-15 second to quench the reaction. Quenching the reaction did not present any difficulties such as subsequent desorption.

The "corrected temperature rise" obtained from the Dickinson extrapolation method in these cases needed an additional minor correction. The details of the correction along with the modified Dickinson method are presented in Chapter III.

4. Liquid Sampling

After each matched pair of chemical and electrical measurements, a sample was removed and weighed before analyzing for the acid gas content. To remove a sample the vent valve was closed and nitrogen was introduced into the calorimeter via port 7 (see Figure 2) until the pressure as indicated by the manometer was 20 to 30 kPa. The three-way ball valve was positioned for liquid flow out of the calorimeter. On opening the valve on the sample line liquid was forced through the fritted glass cylinder and out of the calorimeter. Approximately 12 ml were collected each time.

The first 2 ml collected (in a separate bottle), washed out the line and the next 10 ml were used for analysis. The mass of the 12 ml of solution removed was determined using a gravimetric balance accurate to 0.0001 g.

To complete the process, the nitrogen was then vented from the calorimeter. The valve on the sample line was opened and the small amount of liquid left in the line was blown down into the calorimeter with nitrogen from a separate source. The sample line valve and the three-way valve were then placed in the closed position.

When the CO_2 data at 25°C were being collected the 10 ml sample removed was collected in a 10 ml volumetric flask. This was done for the 2.0 N, 3.5 N and the 5.0 N amine solutions used. With this information plots of the density of the loaded solutions versus α were prepared for CO_2 and are presented in Chapter IV. By comparing the density of the unloaded amine solution measured in this work with the values available in the literature[10,29] it is safe to assume the density data presented here are reliable to within 5% or less.

5. Filling, Emptying and Cleaning of Calorimeter

In filling, emptying and cleaning the calorimeter the service port was used. Oil was removed from the bath until the oil level was a little below the calorimeter lid. The plug of the service port was removed and a piece of 1/8 inch O.D. stainless steel tubing was inserted through the port and extended to the bottom of the calorimeter.

To fill the calorimeter the valve on the vent line was opened. The other end of the tubing was inserted into a filling bottle. Amine solution (or cleaning liquid) was forced into the calorimeter by applying N_2 pressure above the liquid in the filling bottle.

In emptying the calorimeter the same set-up was used but now the vent valve was closed and N_2 pressure was applied above the liquid in the calorimeter. In this case the discharged solution was collected in the filling bottle.

For cleaning of the calorimeter distilled water was pushed into the calorimeter using the technique described for filling. N_2 was bubbled through the fritted glass cylinder to ensure proper rinsing inside the calorimeter and the liquid was removed using the procedure described for emptying. The valves on the liquid sample line were momentarily opened as the cleaning liquid was discharging, to wash out the sample line.

Using the same procedure, the calorimeter was then rinsed out with acetone. After the acetone was discharged the valves on the vent line and the sample line were placed in the open position and N_2 was flowed through the calorimeter for approximately 1 hour to evaporate the last traces of acetone in the calorimeter.

Once the calorimeter was filled after cleaning, the service port was sealed again and the oil level in the bath restored to its original position.

Note for the amine solutions containing H_2S, N_2 was bubbled through the solution for several hours to desorb the H_2S before discharging the liquid from the calorimeter.

6. Liquid Analysis

In this work only direct titration methods were used for the chemical analysis of the acid gases. Methods which rely on the evolution of CO_2 and H_2S were not tried because these methods are known[22] to be unreliable when the sample size is small as it is here (10 ml). As there were virtually no experimental data on the heat of solution or the heat capacity of the loaded solutions available in the literature, the titration methods could not be checked by the common method of reproducing available data. Most of the titration methods were tested by Nasir[22] and the ones used by Nasir[22] were employed in this work.

Several minor modifications to the procedures were necessary as the concentration of acid gas in this work was larger than that encountered by Nasir[22]. The details of the analysis are presented below.

a) CO_2 Determination

CO_2 by precipitation as $BaCO_3$[9]:

The CO_2 in an aliquot portion of the sample was precipitated as barium carbonate ($BaCO_3$) in the presence of excess barium chloride ($BaCl_2$). The solution was filtered and the $BaCO_3$ precipitate was titrated with 0.1 N hydrochloric acid using modified methyl orange (Methyl Orange - Xylene Cyanol solution) indicator.

Procedure: About 30 ml of distilled water was heated in a 250 ml Erlenmeyer flask. Once the water had started boiling approximately 10 g of solid $BaCl_2$ was added. The flask was swirled to dissolve the $BaCl_2$.

At this point two alternatives were available depending on the value of α. For the $BaCO_3$ to precipitate the medium must be basic. If α was approximately 0.3 or less, a 1 ml sample of the solution was added slowly to the $BaCl_2$ solution with a 1 ml syringe. The DEA in the sample was sufficient base for the precipitation to take place.

If α was greater than about 0.3, a few drops of 10 N DEA were added to the $BaCl_2$ solution to make it basic before injecting the 1 ml sample. If this was not done CO_2 was lost by evolution from the sample as it contacted the $BaCl_2$ solution. With α greater than 0.3, the DEA in the sample was not enough to provide the basicity needed for the precipitation to occur.

In either case, once the sample was added and the precipitate formed the flask was stoppered, cooled under cold tap water and left overnight for the precipitate to settle. Next day the precipitate was filtered by gravity using a 70 mm filtering funnel and one 12.5 cm No. 42 Whatman ashless filter paper. The flask containing the precipitate was washed with distilled water. The wash water was transferred to the filter paper.

The precipitate and filter paper were washed until the filtrate was no longer basic as indicated by pH paper.

The filtrate was then discarded. During the early stages of this work some precipitate was noticed in the filtrate. This was investigated and found to be caused by the CO_2 in the air, so it was ignored thereafter.

The filter paper with the washed precipitate was transferred to the Erlenmeyer flask which had the precipitate previously and about 50 ml of distilled water was added to it. The contents of the flask were swirled with a magnetic stirrer until the filter paper was pulverized. About 5 drops of modified methyl orange indicator (Methyl Orange - Xylene Cyanol solution) were added to the flask and the mixture titrated with approximately 0.1 N hydrochloric acid. The mixture was titrated to a grey end point. Any barium carbonate precipitate sticking to the sides of the flask was washed down with distilled water and the titration continued to the same grey end point.

b) H_2S Determination:

The method is that outlined by several authors[2,35] and used by Garst & Lawson[11]. An aliquot sample was put into acidified iodine solution. Excess iodine was back titrated using standard sodium thiosulphate solution. Garst and Lawson[11] recommended 18 moles of H_2SO_4 per mole of DEA for the acidification of the iodine. Because of the higher α values encountered in this work an investigation was undertaken and it was found that 18 equivalents of H_2SO_4 per mole of DEA gave more consistent results over this range of α's, namely 0 to 0.90.

Furthermore, Belcher and Nutten[2], and Vogel[35] emphasize that the concentration of sulphide must be kept below 0.02 N. The method utilizes the reversible reaction[35]

$$H_2S + I_2 \rightleftharpoons 2H^+ + 2I^- + S.$$

With solutions more concentrated than about 0.02 N, the precipitated sulphur encloses a portion of the iodine, and this escapes the subsequent titration with the sodium thiosulphate solution. The concentration was kept below 0.02 N by increasing the volume of the acidified iodine with distilled water.

Procedure: First of all a guess of the value of α must be made. This was easily done by simply noting the time for which H_2S was bubbled for that particular sample. Three different quantities of 0.1 N standard iodine were used depending on the value of α expected. For α between 0 and 0.20, 20 ml were used for α between 0.2 and 0.7, 50 ml were used and for α greater than 0.7, 100 ml were used. (Note for all values of α encountered 100 ml of iodine would have sufficed but excessive amounts of iodine and thiosulphate would be used up).

The required volume of iodine solution was pipetted into a 500 ml Erlenmeyer flask. The proper excess of sulphuric acid for the size of amine sample aliquot was added. The ratio of sulphuric acid was 18 equivalents of H_2SO_4 per mole of DEA. Based on the estimate of α, distilled water was added to the acidified iodine to ensure that the final concentration of sulphide was less than 0.02 N

once the sample was added to the acidified iodine. (Note the sample could not be diluted by adding it to water because H_2S would be lost on contact of the sample with the water.)

A 1 ml sample was then injected with a syringe into the acidified iodine while swirling the flask. The excess iodine was back titrated with standard 0.1 N sodium thiosulphate solution to a light yellow colour. About 5 ml of 0.2 percent starch indicator solution was added and the titration continued to the change from blue-black to a water-white colour.

c) Amine Determination:

The amine concentration in the liquid was determined by titration of an aliquot of the sample with about 0.1 N sulphuric acid solution using methyl red as an indicator.

Procedure: 5 ml of the sample solution was pipetted into a 125 ml Erlenmeyer flask. A few drops of methyl red indicator were added until the colour was distinctly yellow. The solution was then titrated using approximately 0.1 N sulphuric acid. The end point was indicated by change in colour of the solution from yellow to pink.

CHAPTER III

DATA REDUCTION

Several corrections and reductions were needed to convert the raw data into the desired results. In this chapter the corrections required are explained in Section A, and the major reductions used are developed and presented in Section B.

A. Evaluation of the "Corrected Temperature Rise"

In isoperibol calorimetry, the temperature change of the calorimeter during the main period of an experiment is generally not determined solely by the amount of heat liberated or absorbed by the process under investigation. A certain part of the change is due to heat exchange with the environment and to extraneous thermal effects within the calorimeter, such as heat of stirring, joule heating by an electrical thermometer, etc. The term "corrected temperature rise" is defined as the temperature change which the calorimeter would have experienced in the absence of these pertubations (neglecting thermal gradients in the calorimeter, the effect of which is minimized by the method of comparative measurements.) This term, multiplied by the energy equivalent of the calorimeter, gives the amount of heat attributable to the process under investigation.

Dickinson[7] described a method of calculating the "corrected temperature rise" wherein tangents to the time-temperature curves at the beginning and end of the main

period are extrapolated to a defined time such that the difference of their values at that time is equal to the corrected temperature rise. This "extrapolation time" is determined from graphical integration of the time-temperature curve during the main period.

The validity of the "corrected temperature rise" as a means of comparing two experiments depends on certain characteristics of the design of the calorimeter and of the experiment. These include particularly the requirements that temperature gradients within the calorimeter during the initial and final periods be sufficiently similar during the two experiments, and that the measuring instruments measure a temperature which gives a valid measure of the heat exchange with the environment during the main period, at least on a relative basis for the two experiments.

1. General Derivations

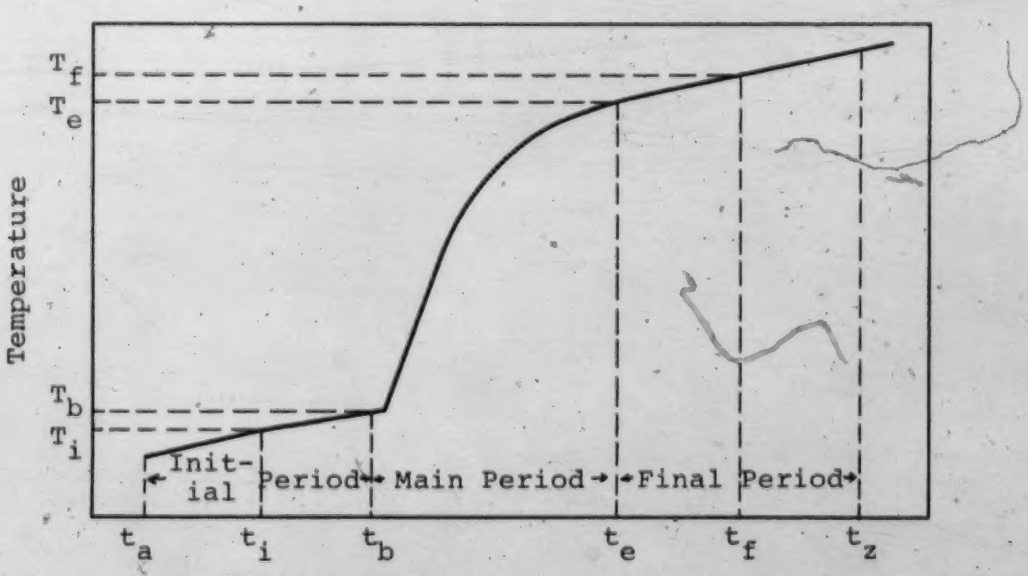


FIGURE 5. Typical Time-Temperature Curve for a Calorimetric Experiment

For a typical calorimetric experiment let the temperatures of the calorimeter during the initial, main, and final periods be designated by T_1, T_2 and T_3, respectively. Subscripts 1 and 3 are also used to denote extrapolations into the main period of the equations describing T for the initial and final periods. The rate of change of the temperature during the initial and final periods is assumed to be described by Newton's law,

$$g = dT/dt = u + k\ (T_j - T) \qquad (2)$$

where $$u = p/\varepsilon \qquad (3)$$

Here p is the sum of all constant thermal powers in the calorimeter, due to stirring, evaporation, etc., ε is the energy equivalent of the calorimeter and its contents, k is the thermal leakage modulus, and T_j is the effective jacket temperature. A convergence temperature T_∞, which T approaches with increasing time, may be obtained by setting $dT/dt = 0$ in Equation (2) and solving for T:

$$T_\infty = T_j + u/k \qquad (4)$$

Substitution of Equation (4) into (2) gives

$$g = dT/dt = k\ (T_\infty - T) \qquad (5)$$

Integration of Equation (5) for T_1 and T_3 gives

$$T_1 = T_\infty - (T_\infty - T_b)\ \exp\{-k\ (t-t_b)\}, \qquad (6)$$

$$T_3 = T_\infty - (T_\infty - T_e)\ \exp\{-k\ (t-t_e)\}, \qquad (7)$$

where T_b and T_e are the temperatures at the times t_b and t_e, which represent the beginning and end of the main period.

In the ensuing treatment, it will be assumed that u, k and T_j are constant. In practice this assumption is almost always made and although it is never strictly true, the net effect of the deviations from it can be made very small if similar conditions are used for the two experiments.

That component of the temperature change during the main period which is due to heat exchange with the environment and to the constant thermal powers p within the calorimeter is also described by Equation (5). Hence the corrected temperature rise ΔT_{corr} is given by

$$\Delta T_{corr} = T_e - T_b - \delta T, \tag{8}$$

where

$$\delta T = k \int_{t_b}^{t_e} (T_\infty - T_2)\,dt \tag{9}$$

The thermal leakage modulus can be obtained from

$$k = (g_i - g_f)/(T_f - T_i) \tag{10}$$

which is derived from Equation (5); g_i and g_f are the values of dT/dt at the mean temperatures T_i and T_f of the initial and final periods. The convergence temperature can also be obtained by rearranging (5)

$$T_\infty = T_f + g_f/k = T_i + g_i/k \tag{11}$$

Equations (6), (7), and (8) are exact insofar as the basic assumptions - that u, k, and T_j are constant - are valid. Because the exponents $k(t-t_b)$ and $k(t-t_e)$ are generally quite small, (6) and (7) may be very closely approximated by quadratic equations which are easier to

handle. It is still easier and common practice, however, to fit the time-temperature curve of the initial and final periods to straight lines,

$$T_1 = T_b^* + g_i^* (t-t_b), \tag{6*}$$

$$T_3 = T_e^* + g_f^* (t-t_e), \tag{7*}$$

graphically. The "corrected temperature rise (linear)" is then defined as

$$\Delta T^*_{corr} = T_e^* - T_b^* - \delta T^* \tag{8*}$$

where

$$\delta T^* = k^* \int_{t_b}^{t_e} (T_\infty^* - T_2)\, dt \tag{9*}$$

$$k^* = (g_i^* - g_f^*)/(T_f - T_i) \tag{10*}$$

$$T_\infty^* = T_f + g_f^*/k^* = T_i + g_i^*/k^* \tag{11*}$$

With the above equations and the time-temperature curve ΔT^*_{corr} can be evaluated. This procedure is referred to as the "integration method". The Dickinson method and its modification designated as "extrapolation methods" will now be considered.

2. Dickinson Method

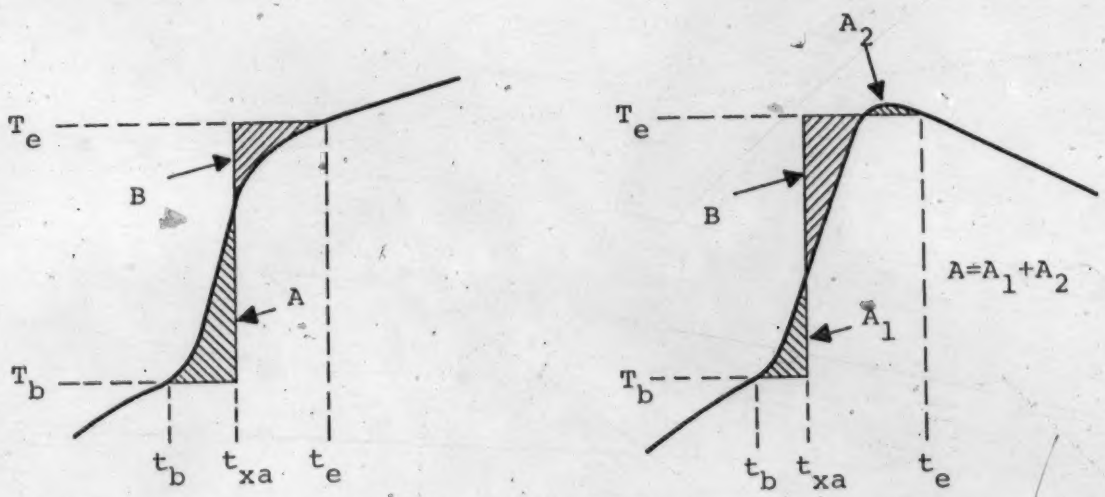


FIGURE 6. Dickinson Extrapolation Method Applied to Two Typical Time-Temperature Curves

Dickinson[7] showed that

$$\Delta T_{corr} = T_{3xa} - T_{1xa} \tag{12}$$

where

$$T_{1xa} = T_b + g_b(t_{xa} - t_b) \tag{13}$$

$$T_{3xa} = T_e + g_e(t_{xa} - t_e) \tag{14}$$

if time t_{xa} is selected so that

$$\int_{t_b}^{t_{xa}} (T_2 - T_b)\,dt = \int_{t_{xa}}^{t_e} (T_e - T_2)\,dt \tag{15}$$

that is, so that areas A and B in Figure 6 are equal. The

proof is as follows. Splitting the integral of Equation (9) into four equivalent components gives

$$\Delta T_{corr} = T_e - T_b - k \left\{ \int_{t_b}^{t_{xa}} (T_\infty - T_b)\,dt - \int_{t_b}^{t_{xa}} (T_2 - T_b)\,dt + \int_{t_{xa}}^{t_e} (T_\infty - T_e)\,dt + \int_{t_{xa}}^{t_e} (T_e - T_2)\,dt \right\} \quad (16)$$

But upon substitution of (15) into (16), the second and fourth integrals cancel, eliminating T_2. Performing the remaining integrations gives

$$\Delta T_{corr} = T_e - T_b - k\,(T_\infty - T_b)(T_{xa} - t_b) - k(T_\infty - T_e)(t_e - t_{xa}) \quad (17)$$

But from Equation (5)

$$g_b = k(T_\infty - T_b) \quad (18)$$

$$g_e = k(T_\infty - T_e) \quad (19)$$

Substitution (18) and (19) into Equation (17) gives

$$\Delta T_{corr} = T_e + g_e(t_{xa} - t_e) - T_b - g_b(t_{xa} - t_b) \quad (20)$$

which upon substitution of (13) and (14) becomes Equation (12).

3. Modified Dickinson Method

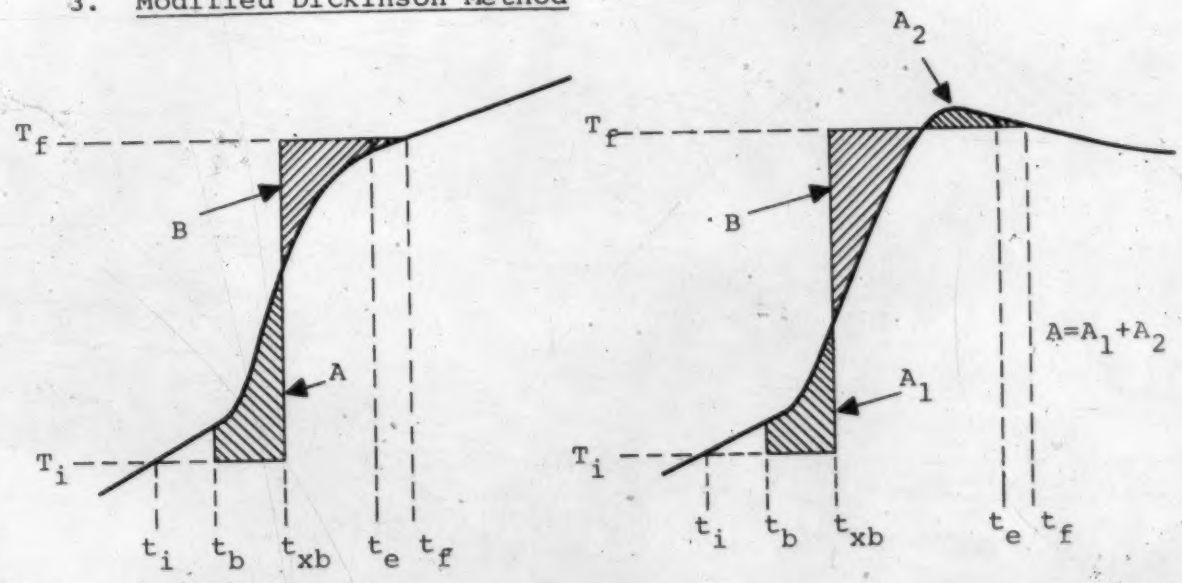


FIGURE 7. Modified Dickinson Extrapolation Method Applied to Two Typical Time-Temperature Curves

Gunn's[12] modification to Dickinson's method gives ΔT^*_{corr} rather than ΔT_{corr} from

$$\Delta T^*_{corr} = T_{3xb} - T_{1xb} \tag{21}$$

where from (6*) and (7*),

$$T_{1xb} = T^*_b + g^*_i\,(t_{xb}-t_b), \tag{22}$$

$$T_{3xb} = T^*_e + g^*_f\,(t_{xb}-t_e), \tag{23}$$

t_{xb} being selected so that

$$\int_{t_b}^{t_{xb}} (T_2-T_i)\,dt = \int_{t_{xb}}^{t_e} (T_f-T_2)\,dt, \tag{24}$$

that is, so that areas A and B are equal in Figure 7. The proof is as follows. Splitting the integral of Equation (9^*) into four components gives

$$\Delta T^*_{corr} = T^*_e - T^*_b - k^* \left\{ \int_{t_b}^{t_{xb}} (T^*_\infty - T_i)\,dt - \int_{t_b}^{t_{xb}} (T_2 - T_i)\,dt \right.$$

$$\left. + \int_{t_{xb}}^{t_e} (T^*_\infty - T_f)\,dt + \int_{t_{xb}}^{t_e} (T_f - T_2)\,dt \right\} \qquad (25)$$

On substituting (24) into (25) the second and fourth integrals cancel, elimination T_2. Performing the remaining integrations gives

$$\Delta T^*_{corr} = T^*_e - T^*_b - k^* (T^*_\infty - T_i)(t_{xb} - t_b) -$$

$$k^* (T^*_\infty - t_f)(t_e - t_{xb}) \qquad (26)$$

From Equation (11^*)

$$g^*_i = k^* (T^*_\infty - T_i), \qquad (27)$$

$$g^*_f = k^* (T^*_\infty - T_f) \qquad (28)$$

substituting of (27) and (28) into Equation (26) gives

$$\Delta T^*_{corr} = T^*_e + g^*_f (t_{xb} - t_e) - T^*_b - g^*_i (t_{xb} - t_b) \qquad (29)$$

Substituting (22) and (23) into (29) gives (21).

This method requires only extrapolation of the linear Equations (6^*) and (7^*).

4. Application of the Modified Dickinson Method.

Throughout this work Equation (29) was used to determine the "corrected temperature rise". For most of the measurements made, g_i^* (that is the slope of the time temperature curve at the mean temperature of the initial period) was practically zero. So Equation (29) reduced to

$$\Delta T^*_{corr} = T_e^* + g_f^* (t_{xb} - t_e) - T_b^* \qquad (30)$$

Because of the nature of the chemical reactions involved and the range of temperatures and normalities investigated the time-temperature curves of the chemical measurements took on a variety of shapes. On the contrary all the electrical measurements produced time-temperature curves with the same relative shape. In order to be consistent in applying Equation (30) for both types of measurements, the following procedure was adopted:

a) time t_{xb} was found graphically such that the areas A and B were equal within 2%,

b) T_e^* the temperature at the end of the main period was taken to be the maximum value achieved on the time-temperature curve,

c) T_f^* the mean temperature of the final period was the point at which the time-temperature curve changed from a curve to a straight line. The straight line portion persisted for a period of 10 to 15 minutes.

d) g_f^* the slope of the time-temperature curve at the mean temperature of the final period (i.e. T_f^*) was

the slope of the straight line portion mentioned in (c).

e) T_b^* the temperature at the end of the initial period, was essentially constant and taken as the value before the calorimeter heater or the gas flow were turned on.

With this convention it was possible to evaluate the "corrected temperature rise" for all the electrical and the majority of the chemical measurements. As mentioned in Chapter II a small percentage of the chemical measurements need an additional correction to the "corrected temperature rise".

With all the electrical measurements and the chemical measurements in which the reaction was not quenched, if the temperature increments during the main period were approximately equal (i.e. 3°C) then g_f^* for all these measurements were also approximately equal. For the chemical measurements exhibiting residual reaction after the time-temperature curve had a negative slope, g_f^* was lower, even though the increment in temperature during the main period was also 3°C. The heat released gradually by the residual reaction offset the rate of heat loss from the calorimeter to the bath. The net result was a small g_f^* compared to the values in the other measurements.

The "corrected temperature rise" ΔT^*_{corr} for these cases was evaluated in the same fashion using Equation (30) and the low value of g_f^* obtained from the time-temperature

curve. Two corrections C_1 and C_2 were added to ΔT^*_{corr} to obtain ΔT^{**}_{corr} which was then used in the subsequent calculations for the heat of solution. C_1 corrected for the low value of g_f^*. C_2 corrected for the fact that the effect of the small amount of heat from the residual reaction was not reflected in ΔT^*_{corr}, but the small amount of gas causing it was showing up in the analysis. The corrections were as follows:

$$C_1 = (g_f^{**} - g_f^*)(t_{xb} - t_e), \tag{31}$$

$$C_2 = (g_f^{**} - g_f^*)(t_t - t_e), \tag{32}$$

and $$\Delta T^{**}_{corr} = \Delta T^*_{corr} + C_1 + C_2 \tag{33}$$

where

g_f^{**} = the value of dT^*/dt at T_f^* for the equivalent electrical measurement, made after the chemical measurement in question,

and $t_t - t_e$ = the time difference between t_e and the instant the reaction is quenched. (Note this time is available from the recorder chart).

The assumption being made here is that g_f^{**} would have been the value of dT^*/dt at T_f^* if there were no residual reaction occurring once the time-temperature curve had a negative slope. (C_1+C_2) accounted for 10% or less of ΔT^{**}_{corr}.

B. Thermodynamic Relations

The thermodynamic relationships needed to reduce the raw data into the differential heat of solution data are developed in this section. The development is broken into two steps. Step 1 represents the differential mixing of the fresh amine solution (i.e. $\alpha = 0$), with the first incremental amount of acid gas; the final composition of the solution being α_1. In this step the temperature of the solution changes from T', the bath temperature, to some value T" which is larger than T'.

Step 2 depicts the addition of the second incremental amount of acid gas which changes the composition of the solution from α_1 to α_2. The temperature of the solution increases from T' the bath temperature, to T". Note T" for Step 2 is assumed to be the same as T" in Step 1 for the sake of simplicity. In the development of the equations, it makes no difference what the final temperature is after mixing, because 1) the equations are general and 2) corrections are applied to refer all quantities back to the initial temperature T'.

The final equations derived are used to calculate 1) ΔH_s the heat of solution at T' and 2) h_α, the specific enthalpy of solution, which can then be used to prepare enthalpy-concentration charts.

Step 1: Addition of acid gas (subscript 1) to fresh amine solution (subscript 2).

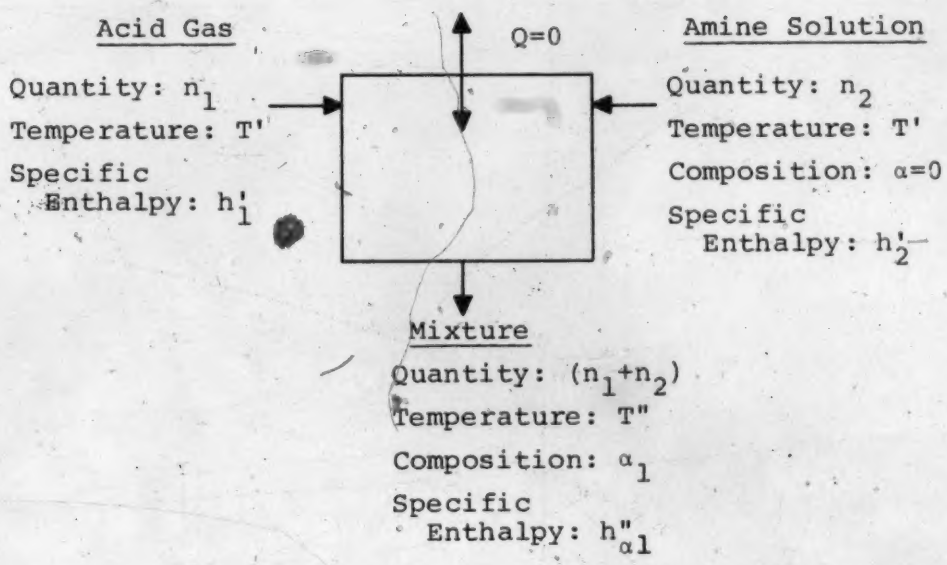


FIGURE 8. Differential Mixing Representation of Step 1.

Application of the first law of thermodynamics to the system, yields

$$h''_{\alpha 1}\,(n_1+n_2) - n_1 h'_1 - n_2 h'_2 = 0 \qquad (34)$$

Correction of the enthalpy of the mixture $h''_{\alpha 1}$ from T" to $h'_{\alpha 1}$ <u>at T'</u> is achieved through the following equation

$$(n_1+n_2)h''_{\alpha 1} - (n_1+n_2)h'_{\alpha 1} = (n_1+n_2)\int_{T'}^{T''} Cp\, dT \qquad (35)$$

where Cp is the heat capacity of the solution.

Rearranging Equation (35) gives

$$(n_1+n_2)h'_{\alpha 1} = (n_1+n_2)h''_{\alpha 1} - (n_1+n_2)\int_{T'}^{T''} Cp\ dT \qquad (36)$$

From Equation (34)

$$(n_1+n_2)h''_{\alpha 1} = n_1h'_1 + n_2h'_2 \qquad (37)$$

Substitution of (37) into (36) gives

$$(n_1+n_2)h'_{\alpha 1} = (n_1h'_1 + n_2h'_2) - (n_1+n_2)\int_{T'}^{T''} Cp\ dT \qquad (38)$$

For the conservation of energy, the heat released on mixing at T' must be

$$\begin{bmatrix}\text{Heat Released}\\ \text{Step 1}\end{bmatrix} = (n_1+n_2)h'_{\alpha 1} - n_1h'_1 - n_2h'_2 \qquad (39)$$

Substitution of Equation (38) into (39) leads to

$$\begin{bmatrix}\text{Heat Released}\\ \text{Step 1}\end{bmatrix} = -(n_1+n_2)\int_{T'}^{T''} Cp\ dT \qquad (40)$$

The quantity on the right hand side of Equation (40) is the energy required to raise the temperature of the solution from T' to T". Call this quantity - Q_1. (i.e. $Q_1 = (n_1+n_2)\int_{T'}^{T''} Cp\ dT$.

If it is assumed that the heat capacity of the solution is approximately the same, over the range $\alpha=0$ to $\alpha=\alpha_1$, as it is for $\alpha=\alpha_1$, then an electrical calibration after mixing is sufficient to determine Q_1. More specifically, if Q_1 causes

a temperature rise ΔT_c for the chemical run, and Q_e causes a temperature rise ΔT_e (where $\Delta T_c = \Delta T_e$) for the electrical run, then

$$Q_1 = \frac{Q_e \Delta T_c}{\Delta T_e} \tag{41}$$

In other words, Q_1 the "chemical" heat released on mixing at T' is obtained via the matched electrical run.

Resubstitution of (40) into (36) gives

$$(n_1+n_2)h'_{\alpha 1} = (n_1 h'_1 + n_2 h'_2) - Q_1 \tag{42}$$

Or $h'_{\alpha 1}$, the enthalpy of the solution per "unit of mixture" is

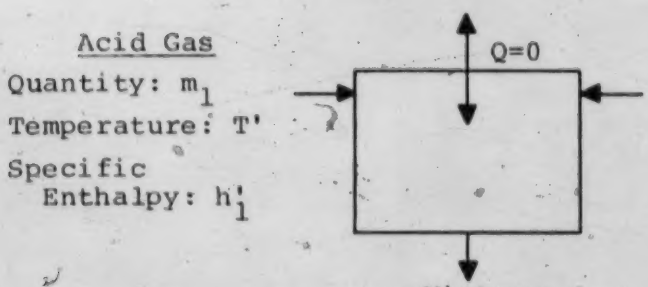
$$h'_{\alpha 1} = \frac{(n_1 h'_1 + n_2 h'_2) - Q_1}{(n_1 + n_2)} \tag{43}$$

The enthalpy of the solution per unit of component 1 is equal to

$$\frac{(n_1+n_2)h'_{\alpha 1}}{n_1} = \frac{(n_1 h'_1 + n_2 h'_2) - Q_1}{n_1} \tag{44}$$

Equations (40) and (41) are used in determining the differential heat of solution as explained in Section C of this Chapter. Equations (43) and (44) are utilized in preparing an enthalpy - concentration diagram which is presented in Chapter IV.

Step 2: Addition of acid gas to the loaded amine solution after a quantity "a" (i.e. liquid sample used for analysis) has been removed.



Acid Gas
Quantity: m_1
Temperature: T'
Specific Enthalpy: h'_1

Amine Solution
Quantity: (n_1+n_2-a)
Temperature: T'
Composition: α_1
Specific Enthalpy: $h'_{\alpha 1}$

Mixture
Quantity: $(n_1+m_1+n_2-a)$
Temperature: T"
Composition: α_2
Specific Enthalpy: $h''_{\alpha 2}$

FIGURE 9. Differential Mixing Representation of Step 2.

Application of the first law of thermodynamics to the system yields

$$(n_1+m_1+n_2-a)h''_{\alpha 2} - [m_1h'_1+(n_1+n_2-a)h'_{\alpha 1}] = 0 \qquad (45)$$

Rearranging Equation (45) gives

$$(n_1+m_1+n_2-a)h''_{\alpha 2} = [m_1h'_1 + (n_1+n_2)h'_{\alpha 1} - ah'_{\alpha 1}] \qquad (46)$$

From Equation (42) of Step 1

$$(n_1+n_2)h'_{\alpha 1} = (n_1h'_1 + n_2h'_2) - Q_1 \qquad (47)$$

Substitution of Equation (47) into (46) gives

$$(n_1+m_1+n_2-a)h''_{\alpha 2} = m_1h'_1+(n_1h'_1+n_2h'_2) - Q_1-ah'_{\alpha 1} \qquad (48)$$

Correction of the enthalpy of the mixture $h''_{\alpha 2}$ from T" to $h'_{\alpha 2}$ <u>at T'</u> is achieved through the following equation

$$(n_1+m_1+n_2-a)(h''_{\alpha 2}-h'_{\alpha 2}) = (n_1+m_1+n_2-a)\int_{T'}^{T''} Cp\ dT \qquad (49)$$

The quantity on the right hand side of Equation (49) is the energy required to raise the temperature of the solution from T' to T". Call this quantity Q_2.

Rearrangement of Equation (49) gives

$$(n_1+m_1+n_2-a)h'_{\alpha 2} = (n_1+m_1+n_2-a)h''_{\alpha 2} - Q_2 \qquad (50)$$

Substitution of Equation (48) into (50) leads to

$$(n_1+m_1+n_2-a)h'_{\alpha 2} = m_1h'_1 + (n_1h'_1 + n_2h'_2) - Q_1 - ah'_{\alpha 1} - Q_2 \qquad (51)$$

For the conservation of energy the heat released on mixing <u>at T'</u> must be

$$\begin{bmatrix}\text{Heat Released}\\ \text{Step 2}\end{bmatrix} = (n_1+m_1+n_2-a)h'_{\alpha 2} - m_1h'_1 - (n_1+n_2-a)h'_{\alpha 1} \qquad (52)$$

Substitution of Equation (51) into (52) gives

$$\begin{bmatrix}\text{Heat Released}\\ \text{Step 2}\end{bmatrix} = (n_1h'_1-n_2h'_2) - Q_1-Q_2-(n_1+n_2)h'_{\alpha 1} \qquad (53)$$

Substitution of (47) into (53) results in

$$\begin{bmatrix}\text{Heat Released}\\ \text{Step 2}\end{bmatrix} = -Q_2 \qquad (54)$$

In the same fashion as Step 1, Q_2 the chemical heat released on mixing <u>at T'</u> is obtained from the matched electrical run.

From Equation (51) the enthalpy of the solution per "unit of mixture" is given by

$$h'_{\alpha 2} = \frac{m_1 h'_1 + (n_1 h'_1 + n_2 h'_2) - Q_1 - a h'_{\alpha 1} - Q_2}{(n_1 + m_1 + n_2 - a)} \qquad (55)$$

The enthalpy of the solution per unit of component 1 is equal to

$$\frac{h'_{\alpha 2}(n_1 + m_1 + n_2 - a)}{(n_1 + m_1)} = [m_1 h'_1 + (n_1 h'_1 + n_2 h'_2) - Q_1 - a h'_{\alpha 1} - Q_2]/(n_1 + m_1) \qquad (56)$$

Equation (54) in conjunction with Equations (40) and (41) are used to prepare a plot of the cumulative heat released versus the moles of acid gas reacted. The differential heat of solution is then obtained from this plot by differentiation. Equations (55) and (56) in conjunction with (43) and (44) are used to prepare the enthalpy concentration chart already mentioned.

If the development of the equations is done for Step 3, the next incremental step, the following equations are obtained.

The enthalpy of the solution per "unit of mixture" is given by

$$h'_{\alpha 3} = [m_1 h'_1 + p_1 h'_1 + (n_1 h'_1 + n_2 h'_2) - Q_1 - a h'_{\alpha 1} - Q_2 - b h'_{\alpha 2} - Q_3]/(n_1 + m_1 + p_1 - a - b) \qquad (57)$$

The enthalpy of the solution per unit of component 1 is equal to

$$\frac{h'_{\alpha 3}\ (n_1+m_1+p_1+n_2-a-b)}{(n_1+m_1+p_1)} = [m_1h'_1+p_1h'_1+(n_1h'_1+n_2h'_2)-Q_1-ah'_{\alpha 1}-bh'_{\alpha 2}-Q_3]/(n_1+m_1+p_1) \qquad (58)$$

where p_1 = incremental amount of acid gas dissolved in Step 3,

b = quantity of sample removed for analysis after Step 2,

and Q_3 = chemical heat released at T' in Step 3.

The form of the equations for the additional steps is obvious from Equations (43), (55) and (57).

In preparing the enthalpy - concentration chart shown in Chapter IV the reference states were chosen to be the pure components at 25°C, (i.e. CO_2 or H_2S gas and fresh DEA solution). With this reference state h'_1 and h'_2 are both zero; this leads to simplifications of Equations (43), (44), (55), (56), (57), and (58). Note this only applies for 25°C.

At the higher temperatures (50°C and 75°C) the enthalpies of the pure components at the respective temperature are needed. For the acid gases the specific enthalpy h_1 was taken from the work of Passut and Danner[24]. In this source the enthalpy of a pure component is expressed as a function of temperature by means of a polynomial equation. The specific enthalpy h_2 of the fresh DEA solution is obtained through integration of the heat capacity data with respect to temperature.

C. Method of Slope[4]

There are two standard methods available to calculate the differential heat of solution. The methods are 1) the method of slope and 2) the method of tangential intercept. In this work the method of slope was used to calculate the differential heat of solution.

In this method the heat released Q is plotted against the mole ratio n_1/n_2 (which is α in this work), then at any point

$$\text{Slope} = \left[\frac{\partial Q}{\partial (n_1/n_2)}\right]_{n_2} = n_2 \left(\frac{\partial Q}{\partial n_1}\right)_{n_2} \qquad (59)$$

where $\left(\frac{\partial Q}{\partial n_1}\right)_{n_2}$ is the differential heat of solution. With this method at any value of n_1/n_2 the slope divided by n_2 is equal to the differential heat of solution.

In this work n_2 the moles of DEA were not constant because a small amount was removed each time a liquid sample was taken. Therefore Q was not plotted versus n_1/n_2. Instead, the cumulative heat released (Q_{cum}) was plotted versus the cumulative moles of gas reacted (n_{cum}). The slope of this plot at each n_1/n_2(or α) was subsequently plotted against α. This gave a relation for the differential heat of solution ΔH_s as a function of α.

To obtain Q_{cum}, the heat released after each step i.e., Q_1, Q_2, Q_3, etc. (from Equations (41) etc.), was added cumulatively. The moles of acid gas reacted in each step were also added cumulatively to obtain n_{cum}. In plotting

Q_{cum} versus n_{cum}, the data were fitted with a least squares polynomial fit with the aid of a computer program. Differentiation of the resulting equation gave ΔH_s values which were unbiased and consistent. The results obtained for each set of data are presented in Chapter IV.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

In this chapter, the experimental results are presented. The material is presented in a combination of graphical and tabular forms.

Section A deals mainly with the experimental data obtained in this work. As this is the first documented measurement of the heats of solution of CO_2 and H_2S in diethanolamine solutions, no experimental data were available for comparison. However, comparisons are made in Section B, between the experimentally determined ΔH_s values and the calculated ΔH_s data available in the literature. Virtually all the data in the literature were obtained via the solubility data. The limitations of the calculated data are brought out in the comparisons.

A. Experimental Results

1) CO_2-DEA System at 25°C.

Four sets of data were collected at a bath temperature of 25°C. Measurements were made with 2.0 N, 3.5 N and 5.0 N DEA solutions. Two sets of data were collected for 3.5 N DEA at 25°C to check the reproducibility. In the early stages of this work the first three sets of data, i.e., 2.0 N, 3.5 N and 5.0 N at 25°C, were collected before the presaturator was installed. The remainder of the data including data set 2 for 3.5 N DEA at 25°C were made with the addition of the presaturator to the equipment.

Figure 10 shows the two sets of data obtained with the 3.5 N DEA. The analogous quantities Q_{cum} and n_{cum} for the 2.0 N and 5.0 N DEA solutions, are tabulated in Appendix 4. On reduction of the 25°C data, linear equations best represented the dependence of the cumulative heat evolved, Q_{cum} on the moles of CO_2 reacted, n_{cum}. The linear relationships were observed for all three normalities investigated at 25°C. The differential heats of solution at 25°C, obtained from the linear equations, are presented in Table I.

TABLE I

DIFFERENTIAL HEAT OF SOLUTION OF CO_2 IN DEA SOLUTIONS AT 25°C

Normality of DEA	$-\Delta H_s$ kJ/mol CO_2	Conditions
2.0 N	71.0	All values valid for maximum α achieved in the measurements, i.e. $\alpha = 0.55$.
3.5 N 1st set	71.9	
5.0 N	71.9	
3.5 N 2nd set	74.6	

At 25°C the differential heat of solution in aqueous diethanolamine solutions is independent of the solution loading α. Secondly, the normality of the diethanolamine solution has virtually no effect on the differential heat of solution at 25°C. As shown in Table I, with the exception of data set 2 for 3.5 N DEA, the

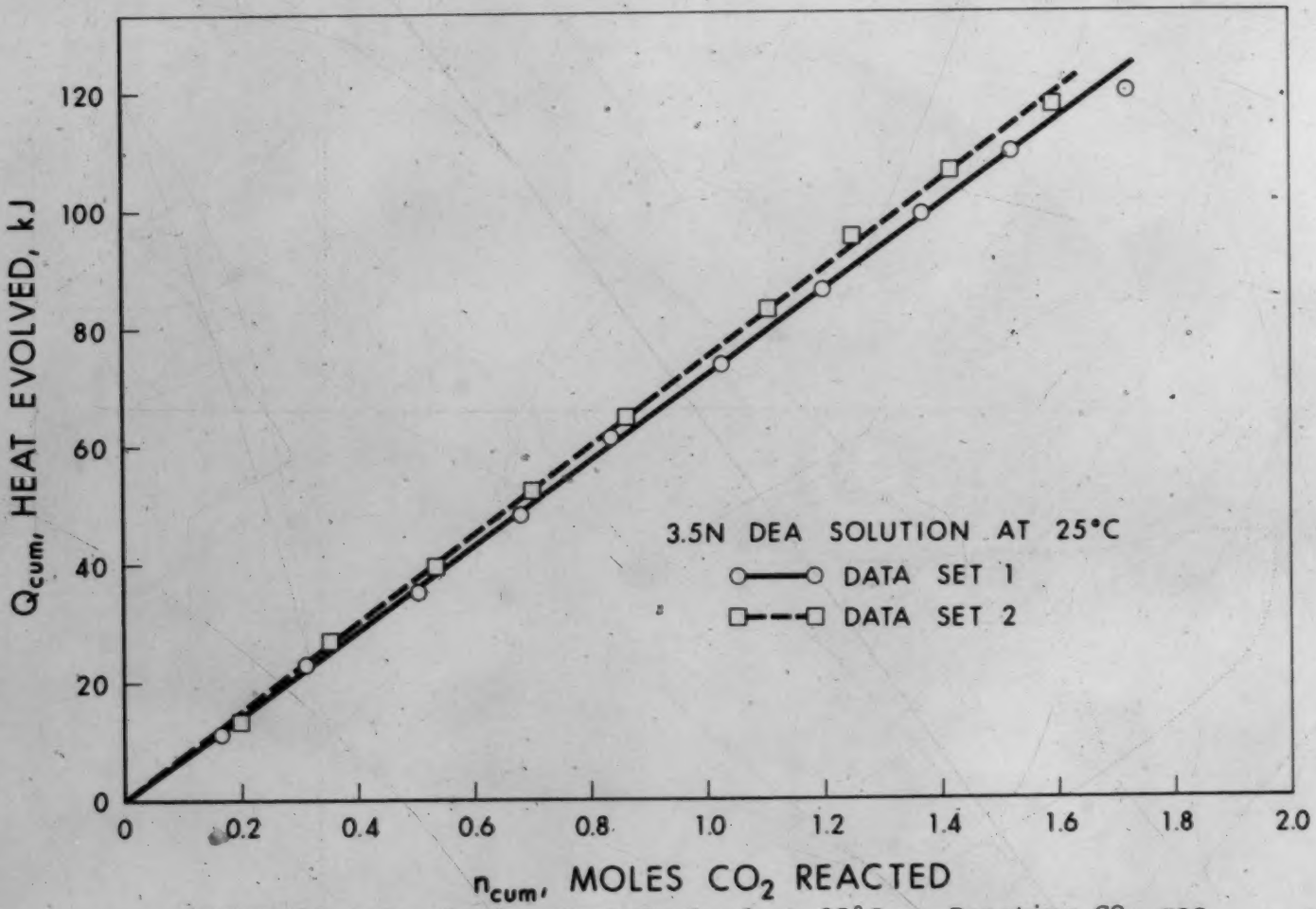


FIGURE 10. Cumulative Heat Evolved at 25°C on Reacting CO_2 gas with 3.5 N DEA Solutions.

differential heat of solution is 71 to 72 kJ/mol CO_2 up to a solution loading of 0.55 moles CO_2/mole DEA.

The difference of 3.8 per cent between data set 1 and data set 2 for the 3.5 N DEA solution, was mainly due to reduced heat losses resulting from the use of the pre-saturator. The value of 74.6 kJ/mol CO_2 for data set 2 is more accurate, and the rest of the values in Table I are probably low by a maximum of 4 per cent. Keeping in mind that the major portion of the 3.8 per cent was related to a change in the equipment, the reproducibility was considered quite good.

The heat capacity data collected at 25°C are presented in Figure 11. For all the work done at 25°C duplicate electrical measurements were made at each α to check the reproducibility of the heat capacity data. An additional electrical measurement was made after the liquid sample was removed. This provided two values of the heat capacity at any particular α, one before and one after removal of the liquid sample. The data for the 5.0 N DEA solution exhibited more scatter than the 2.0 N and 3.5 N DEA solutions. This was partly due to stirring problems encountered with the highly viscous 5.0 N DEA solution. The heat capacities of the uncarbonated amine solutions obtained in this work are within 3 per cent of those given by Union Carbide[29].

2) CO_2-DEA System at 50°C and 75°C.

Figure 12 shows the data obtained for the

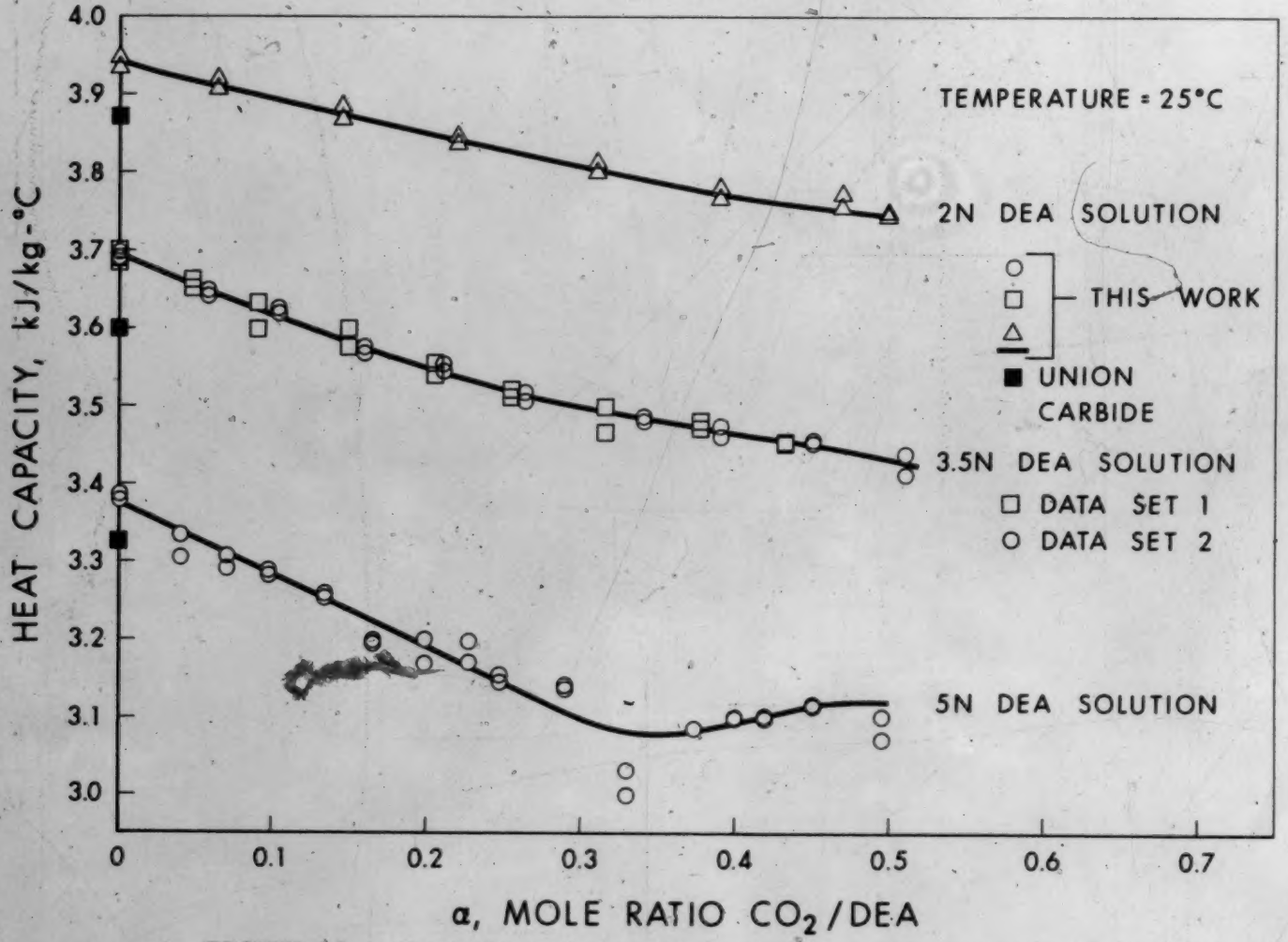


FIGURE 11. Heat Capacities of Carbonated DEA Solutions at 25°C.

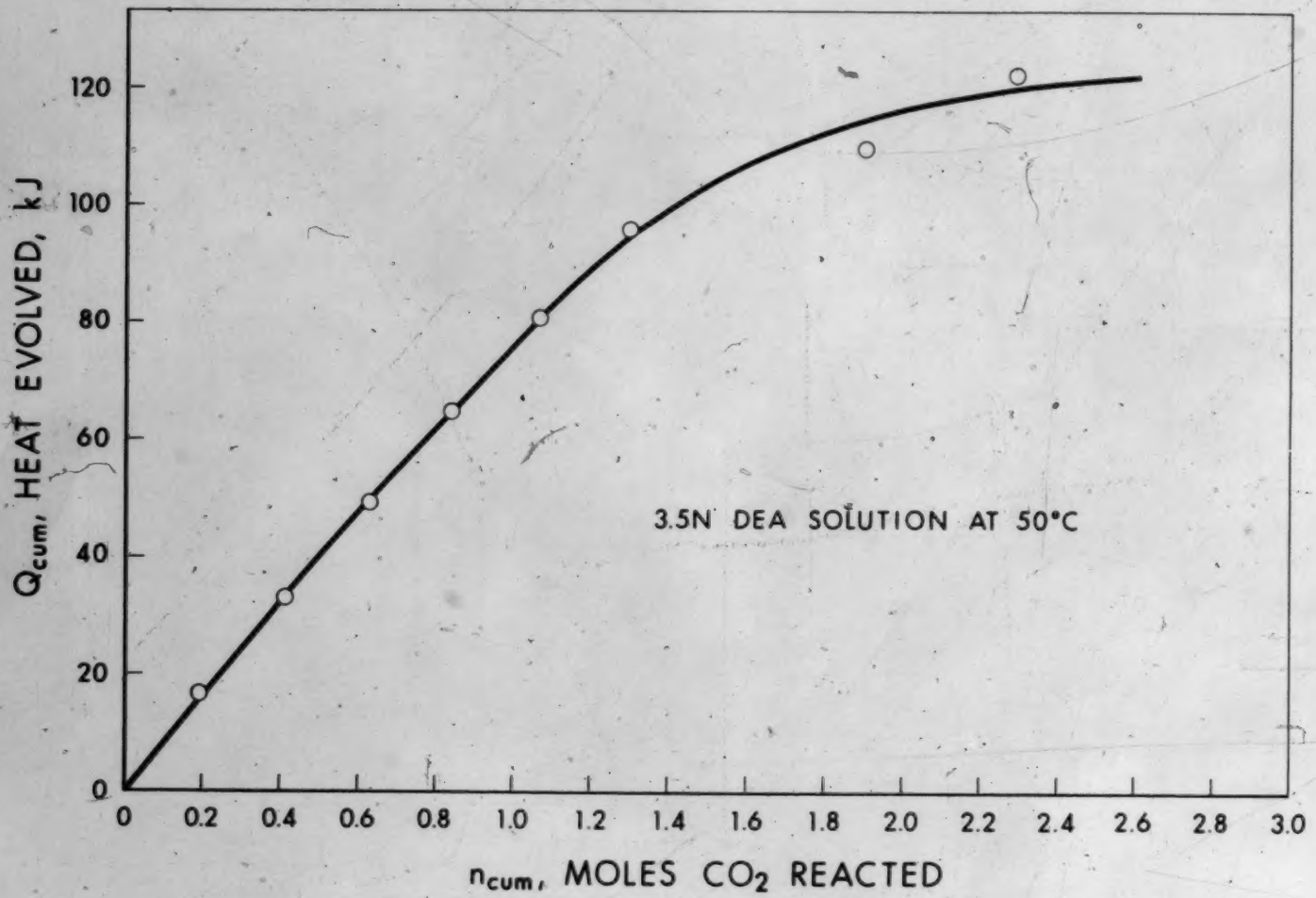


FIGURE 12. Cumulative Heat Evolved at 50°C on Reacting CO_2 gas with 3.5 N DEA Solutions.

cumulative heat evolved versus the moles of CO_2 reacted with the 3.5 N DEA solution at 50°C. The analogous quantities Q_{cum} and n_{cum} for 2.0 N DEA at 50°C and 3.5 N DEA at 75°C are tabulated in Appendix 4. Quadratic equations best represented the data collected at 50°C and 75°C. The ΔH_s values generated by differentiation of the quadratic equations were plotted against α for each set of data. The resulting equations for the differential heat of solution as a function of α are presented in Table II.

TABLE II

DIFFERENTIAL HEAT OF SOLUTION OF CO_2 IN DEA SOLUTIONS AT 50°C AND 75°C

Temperature °C	Normality of DEA	$-\Delta H_s$ kJ/mol CO_2	Conditions Valid for:
50	2.0 N	80.99-56.81 α	Maximum α of 0.42
50	3.5 N	81.97-43.05 α	Maximum α of 0.50
75	3.5 N	93.48-95.88 α	Maximum α of 0.45

At 50°C the differential heat of solution of CO_2 in DEA solutions is a function of the normality and the solution loading α. From Tables I and II it can be seen that ΔH_s is also a function of temperature. The 50°C results for 2.0 N and 3.5 N DEA solutions indicate that the dependence of ΔH_s on normality is not as great as the dependence on temperature.

The heat capacity data for 2.0 N and 3.5 N DEA solutions at 50°C are shown in Figure 13. Duplicate points were not collected at 50°C and 75°C. The analogous heat capacity data for the one normality (i.e. 3.5 N) investigated at 75°C are tabulated in Appendix 4. Figure 14 presents the smoothed heat capacity data for the 3.5 N DEA solution between 25 and 75°C.

3) Other Data CO_2-DEA System

Enthalpy: An enthalpy-concentration chart shown in Figure 15, was prepared for the CO_2-3.5 N DEA system using Equations (44) and (56) etc. With the enthalpy data and the heat capacity data at hand it was possible to perform loop checks to evaluate the internal consistency of the data. The location of the loops are shown in Figure 15 and the results of the loop checks are presented in Appendix 2.

Density: As mentioned in Chapter II density data were collected at 25°C for the three normalities 2.0 N, 3.5 N and 5.0 N investigated. The density data are presented in Figure 16. The densities for the uncarbonated solutions compare with the values of Dow[10] and Union Carbide[29] within 1 per cent but the overall reliability of the density data collected here is 5 per cent or less.

4) H_2S-DEA System at 25°C

Only one set of measurements were made with H_2S. The measurements were made with 3.5 N DEA at 25°C. The quantities Q_{cum} and n_{cum} are tabulated in Appendix 4. On reduction of the data, the differential heat of solution

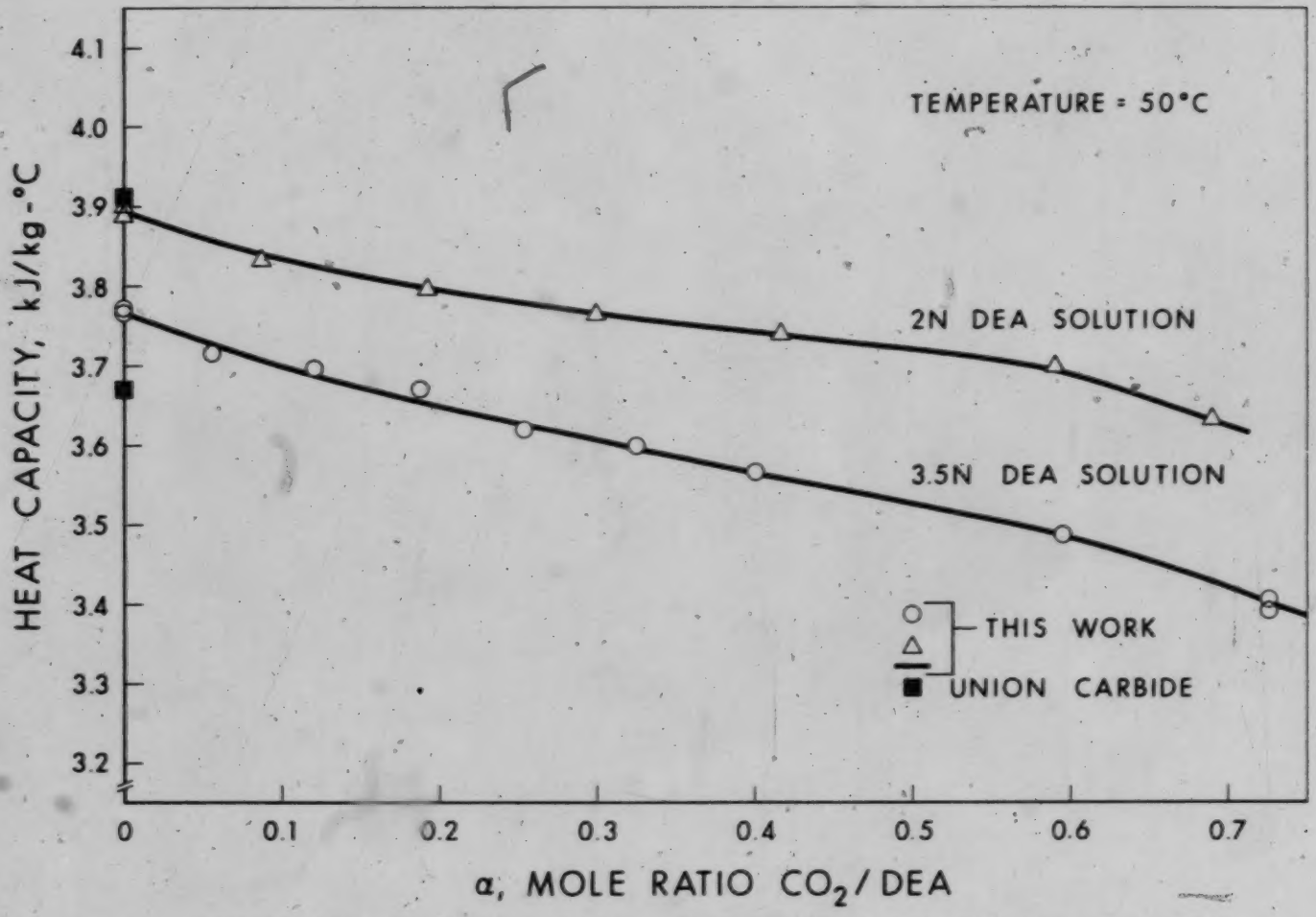


FIGURE 13. Heat Capacities of Carbonated DEA Solutions at 50°C.

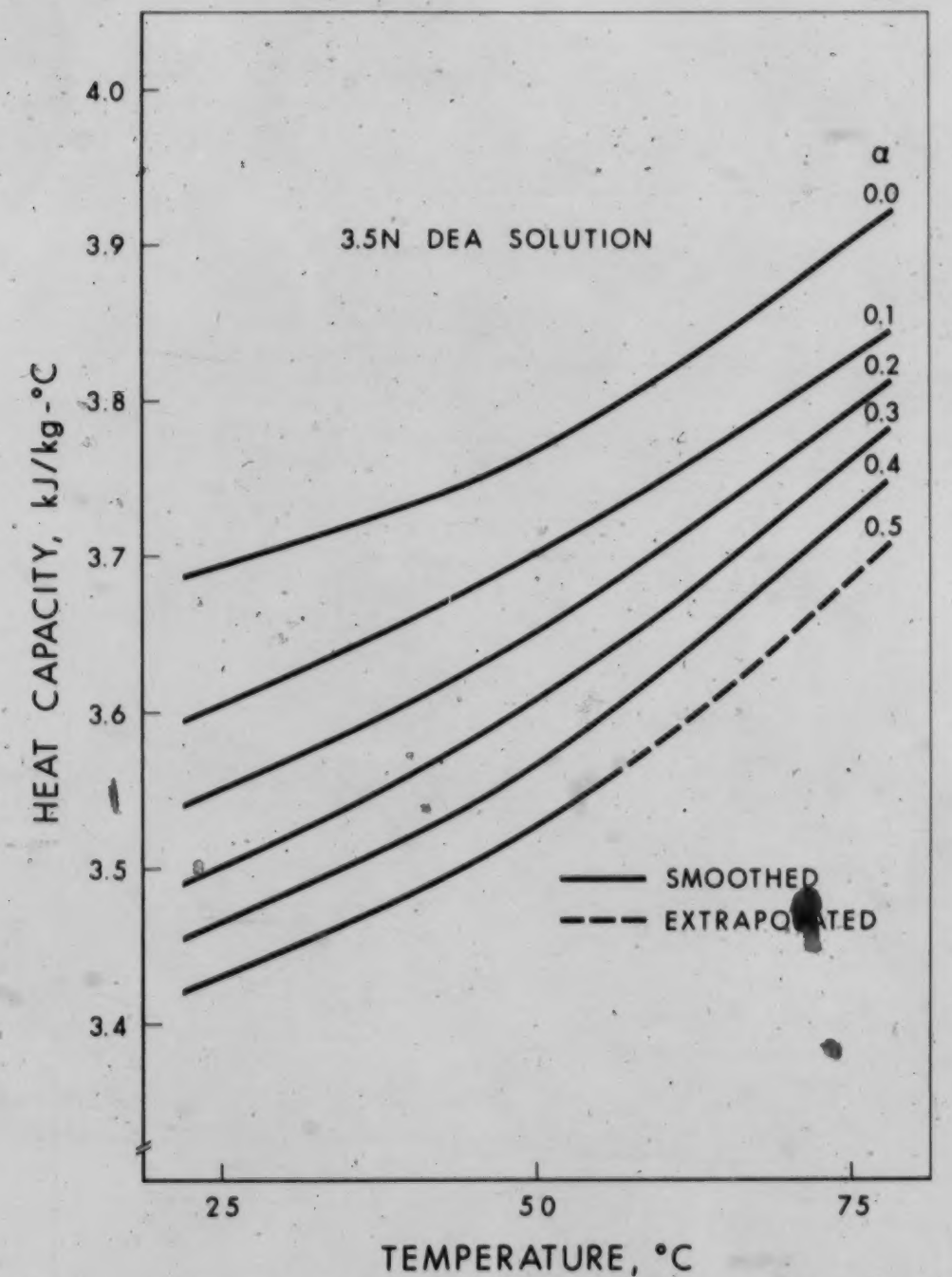


FIGURE 14. Smoothed Heat Capacities of 3.5 N Carbonated DEA Solutions Between 25°C and 75°C.

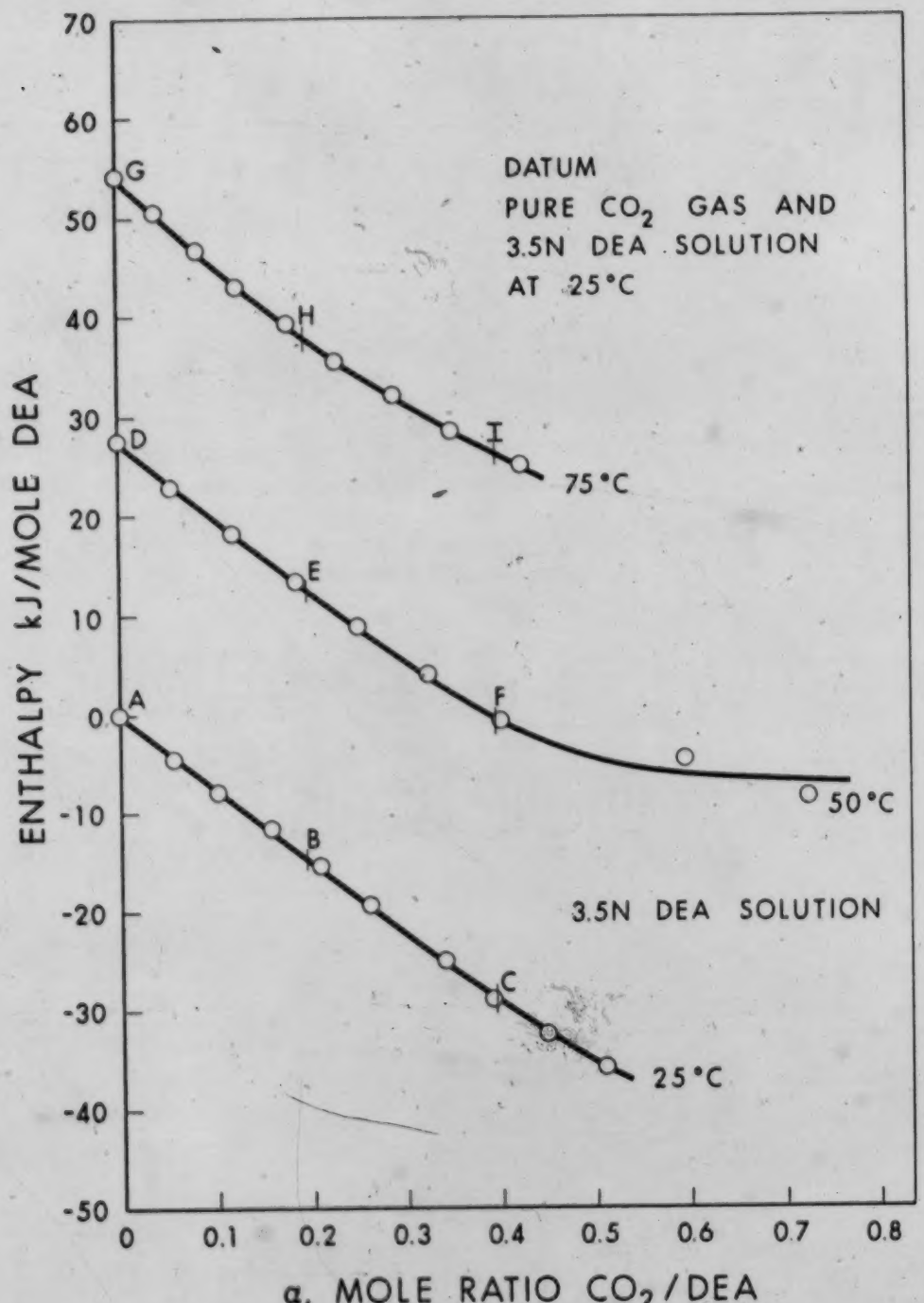


FIGURE 15. Enthalpy-Concentration Diagram for the CO_2-3.5 N DEA System. (Note: A to I define loops for loopchecks presented in Appendix 2)

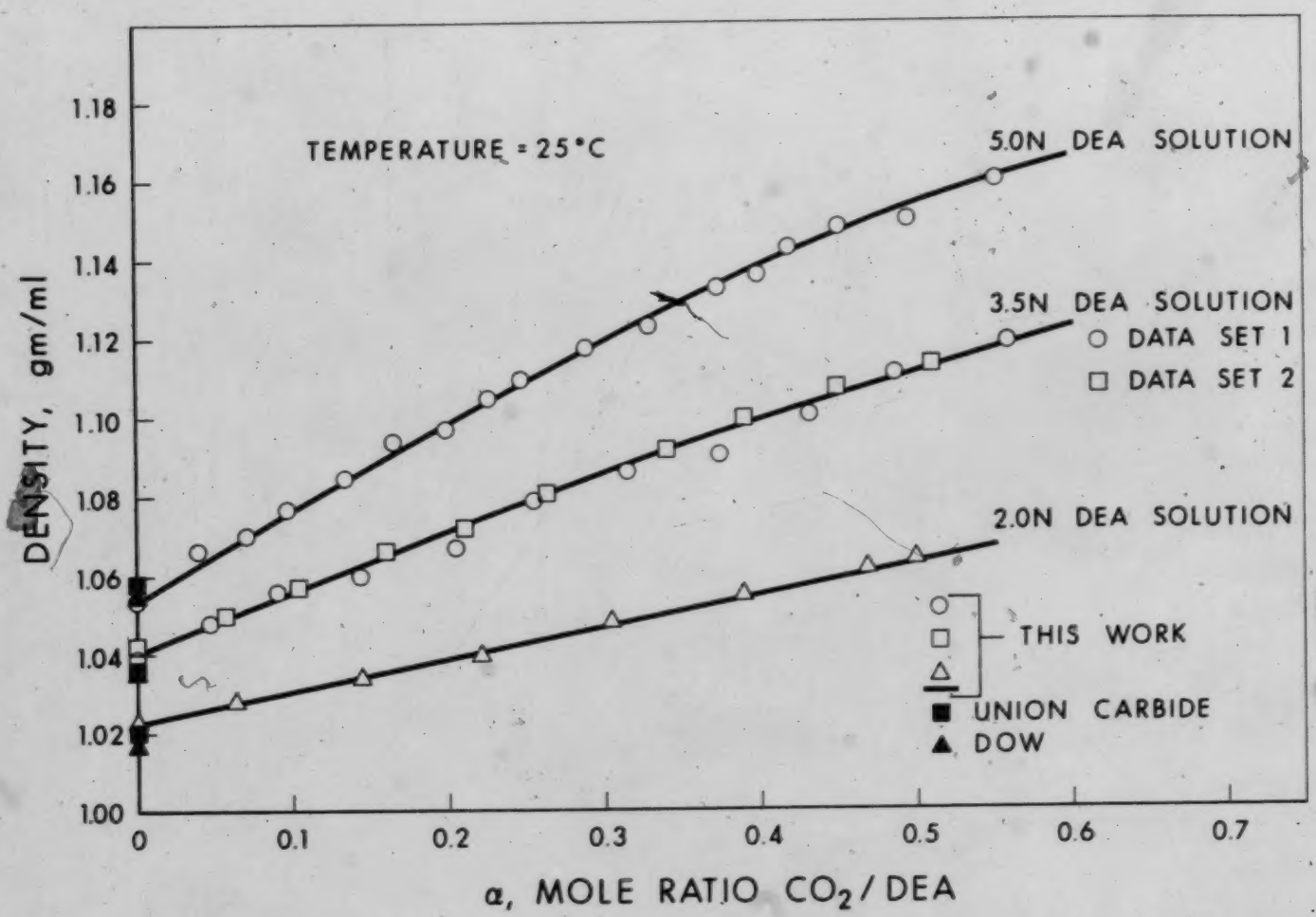


FIGURE 16. Densities of Carbonated DEA Solutions at 25°C.

at 25°C was of the following form:

$$-\Delta H_s = 39.40 + 12.24\ \alpha \qquad (60)$$

kJ/mol H_2S

up to a maximum α of 0.85. In other words, the heat of solution increased slightly with α.

The heat capacity data are tabulated in Appendix 4. Densities were not collected for the 3.5 N DEA solution loaded with H_2S.

B. Comparison of Measured and Calculated Values of ΔH_s.

No documented experimental data on the heat of solution of CO_2 or H_2S in aqueous diethanolamine solutions were found in the literature. ΔH_s values in the literature were obtained via the solubility data, using the analytical methods explained below. Some[3,21] of the values available in the literature were presented without any explanation as to the method used in obtaining them. The analytical methods and the data found in the literature are discussed next.

CO_2-DEA System:

1) Lee et al.[16] employed the following equation to generate approximate values of ΔH_s:

$$\frac{\Delta H_s}{R} = \left[\frac{\partial \ln P_1}{\partial (1/T)}\right]_{x_1} \qquad (61)$$

Plots of lnP versus $\frac{1}{T}$ were prepared by Lee et al., for

solutions ranging from 0.5 N to 8.0 N. ΔH_s values at increments of α equal to 0.2 were calculated for each normality.

The plots of lnP versus $\frac{1}{T}$ were linear within the accuracy of the data for all solutions except that of 0.5 N. By using straight lines the effect of temperature on ΔH_s was "averaged-out". The values of ΔH_s obtained from Equation (61) are applicable over the range of temperature, 0°C to 140°C, used in preparing the plots of lnP versus $\frac{1}{T}$.

In order to compare the values of Lee et al.[16] with the experimental values obtained in this work, average values of ΔH_s over the range 25°C to 75°C were calculated from Tables I and II. The comparison was done for the 3.5 N DEA solution. At each α in question, the arithmetic average of the values of ΔH_s at 25°C, 50°C and 75°C was evaluated. The results of the comparison are shown in Table III.

TABLE III

COMPARISON OF MEASURED ΔH_s VALUES WITH THE CALCULATED VALUES OF LEE ET AL.[16] FOR CO_2 IN A 3.5 N DEA SOLUTION

$-\Delta H_s$, kJ/mol CO_2

α	This Work Average Value 25°C-75°C	Lee et al. Average Value 0°C-140°C	Difference
0.0	83.4	-	-
0.2	74.1	76.3	-3.0%
0.4	64.8	65.4	-1.0%
0.6	-	50.3	-

2) Crynes and Maddox[5] derived an equation for calculating ΔH_s from partial pressure data. The equation is basically the same as Equation (61) in integrated form. They started with the following equation,

$$\frac{d\ln K_a}{dT} = \frac{\Delta H_s^\circ}{RT^2} \tag{62}$$

and integrated with respect to temperature to arrive at

$$\ln \frac{K_a}{K_a^\circ} = \frac{\Delta H_s^\circ}{R} \left(\frac{1}{T_o} - \frac{1}{T_1} \right) \tag{63}$$

By ignoring the change in ratio of amine salt to amine solution with temperature, the equilibrium constant was related to the partial pressure to obtain the final equation

$$\ln \frac{P_o}{P_1} = \frac{\Delta H_s}{R} \left(\frac{1}{T_o} - \frac{1}{T_1} \right) \tag{64}$$

To evaluate the heat of solution at any solution loading α and temperature T, temperatures T_o and T_1 on either side of T were chosen. The corresponding values of P_o and P_1 were then substituted into Equation (64) and ΔH_s evaluated. The evaluations done by Crynes and Maddox[5] were for H_2S in monoethanolamine (MEA) solutions.

To generate ΔH_s values using Equation (64), the smoothed data of Lee et al.[17] were employed here. ΔH_s at 75°C for CO_2 in 3.5 N DEA were evaluated by choosing T_o and T_1 equal to 50°C and 100°C respectively. The values of ΔH_s obtained were 15 to 20% higher than the corresponding measured values at 75°C.

One drawback with methods employing partial pressure data is the subjectivity which may be involved in application of the method. In other words the bias introduced by each author in evaluating the slope of the lnP versus $\frac{1}{T}$ curves.

3) Murzin and Leites[21] calculated values of ΔH_s from the partial pressure data also. The exact procedure was not mentioned. They indicated that ΔH_s was independent of α in the range 0 - 0.2 at 20°C to 90°C. They showed ΔH_s as a decreasing function with increasing normality for the range of α and temperature already mentioned. From their plot of ΔH_s versus normality values of -65.5, -71.6 and -74.6 kJ/mol of CO_2 were obtained for 2 N, 3.5 N and 5.0 N DEA solutions respectively. They mention that ΔH_s decreased with values of α larger than 0.2.

4) One of the earliest references to the heat of solution of CO_2 in aqueous diethanolamine was obtained from the work of Bottoms[3]. The value given by Bottoms[3] (as reiterated by Kohl and Riesenfeld[14]) is 653 Btu/lb_m of CO_2. This corresponds to 66.9 kJ/mol CO_2. Neither the normality, temperature nor the method used in arriving at this value was mentioned.

H_2S-DEA System:

Seeing that only one set of measurements were made with H_2S, only "rough" comparisons can be made because of the non-uniformity of conditions such as normality and temperature. The approximate values given by Lee et al.[18] are average values for 2.0 N DEA and 3.5 N DEA solutions, and apply over the range of temperature 25°C to 120°C. The plots of ln P versus $\frac{1}{T}$ were linear within the accuracy of the data. Table IV shows the measured values for 3.5 N DEA at 25°C obtained from Equation (60) compared with the values of Lee et al.[18]

TABLE IV

COMPARISON OF MEASURED ΔH_s VALUES WITH THE CALCULATED VALUES OF LEE ET AL.[18] FOR H_2S IN DEA SOLUTIONS

	$-\Delta H_s$, kJ/mol H_2S		
α	This Work: 3.5 N DEA 25°C	Lee et al.[18] Average Value of: 2 N and 3.5 N 25°C to 120°C	Difference
0.2	41.8	47.7	-14%
0.4	44.3	43.5	+2%
0.6	46.7	40.0	+14%
0.8	49.7	31.9	+36%

2) Bottoms[3] gives a value of 511 Btu/lb_m (as reiterated by Kohl and Risenfeld[14]), which corresponds to 40.5 kJ/mol H_2S. No mention was made as to the normality, temperature nor the method used in arriving at this value.

SUMMARY AND CONCLUSIONS

1) An adiabatic Dewar-type calorimeter for the direct determination of the differential heat of solution was designed and built.

2) The differential heat of solution of CO_2 in aqueous DEA solutions was determined experimentally at 25°C, 50°C and 75°C. The normality of the DEA solutions used were 2.0 N, 3.5 N and 5.0 N respectively.

3) At 25°C, the differential heat of solution was independend of normality and solution loading. At 50°C and 75°C the differential heat of solution was a function of normality and solution loading. Also, as the temperature increased ΔH_s showed a stronger dependence on temperature than on normality.

4) The heat capacities of the loaded amine solutions were measured for all normalities and at all temperatures used in this work.

5) Density data at 25°C were determined for the CO_2-DEA system for normalities of 2.0, 3.5 and 5.0 respectively.

6) An enthalpy-concentration diagram for the CO_2-3.5 N DEA system was prepared.

7) The H_2S-DEA system was investigated at one set of conditions only. A 3.5 N DEA solution at 25°C was used. The differential heat of solution of H_2S in 3.5 N DEA showed a very slight dependence on solution loading α. Heat capacity data were also obtained.

8) Limited comparisons were made between the experimental ΔH_s values of this work and the calculated ΔH_s data available in the literature. The comparisons indicate the drawbacks involved in obtaining heat of solution data by differentiation of partial pressure solubility data.

9) It appears that if the differential heat of solution were measured at higher solution loadings than those achieved in this work, it would decrease rapidly and approach some fixed value asymptotically.

RECOMMENDATIONS FOR FUTURE WORK

1. More measurements should be conducted with H_2S to confirm the validity of the single data set collected here, and to cover the range of conditions encountered in practice.

2. A new thermistor bridge should be built so that the battery voltage does not have to be adjusted during a run.

3. If possible, a method should be developed to quench the chemical reaction immediately after the gas flow is terminated, without disturbing the temperature of the system.

4. With the present scheme, a small amount of heat is removed by the gas flowing out of the calorimeter. A recycle system aimed at eliminating this loss, should be considered for delivering the gas to the calorimeter.

5. Higher solution loadings can be achieved by operating the calorimeter under pressure. The possibility of operating the calorimeter under pressure should be investigated.

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APPENDIX 1

CALIBRATIONS

Calibration Data for Model 8163 Platinum Resistance Thermometer Serial No. 1724252

The thermometer was calibrated by the National Research Council in June 1969 for use in the range 90.188 K ≤ T ≤ 773.14 K (-182.962°C to 500.00°C) on the International Practical Temperature Scale of 1968. Temperature is measured in terms of the resistance ratio, $W = R/R\ (0°C)$.

For $90.188\ K \leq T \leq 273.15\ K$

$$W = Wcct + dW \tag{65}$$

where Wcct is a reference function, independent of any particular thermometer, and dW is a deviation function.

$$dW = A4t + C4(t-100)t^3 \tag{66}$$

For $0°C \leq t \leq 630.74°C$

$$t = t' + dt' \tag{67}$$

where t' is determined by

$$W = 1 + At' + B(t')^2 \tag{68}$$

and

$$dt' = 0.045\ (t'/100)\left(\frac{t'}{100} - 1\right)\left(\frac{t'}{419.58} - 1\right) x\left(\frac{t'}{630.74} - 1\right) \tag{69}$$

The coefficients in the above relations were found by the National Research Council using fixed-point calibrations i.e. triple point of water, the steam or tin point and the zinc point using continuous thermometer currents of 1 and 2 mA.

Coefficients

	0 mA	2 mA
A	3.98556×10^{-3}	3.985539×10^{-3}
B	-5.87663×10^{-7}	-5.87773×10^{-7}
A4	8.3280×10^{-7}	7.9460×10^{-7}
C4	2.2020×10^{-14}	2.4150×10^{-10}

$R(0^{\circ}C) = 25.5169$ ohms

B. Calibration of Calorimeter and Thermistors

1. Method

The calorimeter and thermistors were calibrated with distilled water as the standard reference material. Water was chosen for the following reasons:

1) its availability in a pure state,
2) numerous measurements of its heat capacity are available in the literature, and
3) its similarity in thermal properties to the diethanolamine solutions.

One litre of distilled water was weighed and charged to the calorimeter. Known amounts of electrical energy were supplied by means of the calorimeter heater to raise the temperature of the water by approximately 1°C, 2°C, 3°C, 4°C and 5°C respectively. Values for the heat capacity of water were obtained from Perry[25] and were used to calculate the exact increase in temperature. The "corrected temperature rises" in millivolts were evaluated from the recorder chart, using the modified Dickinson

method, explained in Chapter III. ΔV values in millivolts (mV) were then plotted versus ΔT values in degrees Celsius (°C), and equations were generated to represent the data.

2. Data

A total of four calibrations were carried out. The calorimeter and thermistors were calibrated at bath temperatures of 25°C, 50°C and 75°C respectively. Two calibrations were done at 25°C. The second calibration was done several months after the first; therefore it was performed after data had been collected at 50°C and 75°C. The second calibration at 25°C was essentially identical to the first.

The actual data points are shown in Table V.

TABLE V

CALIBRATION DATA FOR CALORIMETER AND THERMISTORS

Bath Temperature °C	ΔV mV	Calculated ΔT °C
25 First calibration 21st July, 1975	13.60	1.403
	23.40	2.425
	30.05	3.090
	36.20	3.771
	48.25	4.997
50	13.97	1.762
	18.44	2.371
	27.06	3.516
	34.64	4.562
	41.92	5.562
75	4.83	1.079
	8.84	2.003
	12.97	2.999
	17.07	3.982
	20.53	4.839

Bath Temperature °C	ΔV mV	Calculated ΔT °C
25	11.65	1.210
Second calibration	22.90	2.368
24 November, 1975	32.35	3.355
	41.30	4.292
	49.65	5.170

The data are shown graphically in Figure 17. From the above values the following equations were established.

At T = 25°C

$$\Delta T\ (°C) = \frac{\Delta V(mV) - 0.1}{9.6364} \qquad (70)$$

At T = 50°C

$$\Delta T\ (°C) = \frac{\Delta V(mV) - 1.0}{7.3778} \qquad (71)$$

And at T = 75°C

$$\Delta T\ (°C) = \frac{\Delta V(mV) - 0.5}{4.1600} \qquad (72)$$

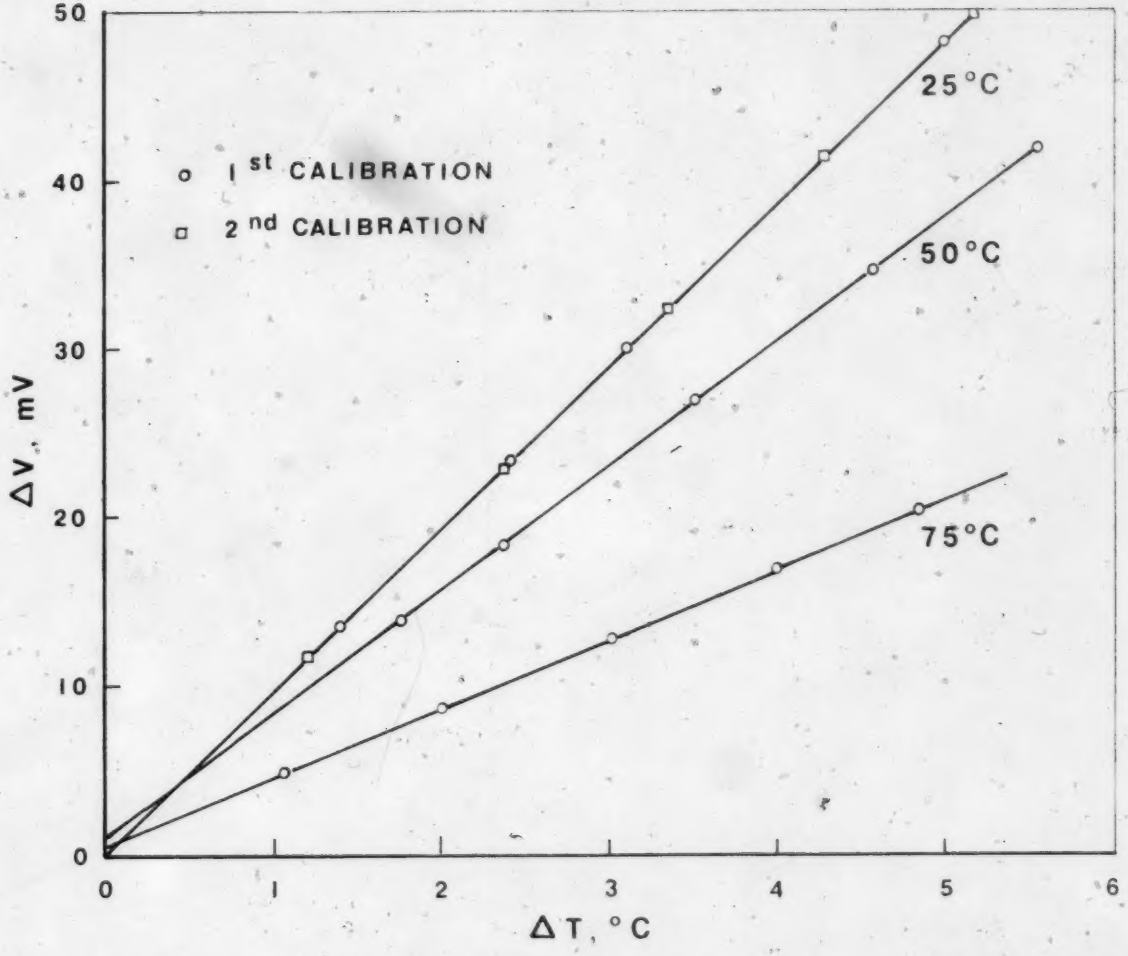

FIGURE 17. Calibration Data for Calorimeter and Thermistors.

APPENDIX 2

LOOP CHECKS

A. Thermodynamic Consistency Checks

The specific enthalpy data h_α (Figure 15) and the smoothed heat capacity data Cp (Figure 14) were used to test the internal consistency of the experimental data. The location of the loops is shown in Figure 15. The enthalpy change along different paths and the percent deviation are given in Table VI.

The formula used in computing the percent deviation around a loop is the following:

$$\text{Percent Deviation} = \frac{\sum \Delta h_i}{\sum |\Delta h_i|} \times 100 \qquad (73)$$

TABLE VI

CONSISTENCY CHECKS ON THE CO_2- 3.5 N DEA SYSTEM

Loops	Δh kJ/mol	$\sum \lvert\Delta h\rvert$ kJ/mol	Percent Deviation
A-B-E	+12.7		
E-D-A	-12.8		
A-B-E-D	-0.1	84.7	-0.1
B-C-F	+13.5		
F-E-B	-14.1		
B-C-F-E	-0.6	82.6	-0.7
D-E-H	13.6		
H-G-D	-12.2		
D-E-H-G	+ 1.4	87.8	+1.6
E-F-I	+15.3		
I-H-E	-16.4		
E-F-I-H	- 1.1	82.5	-1.3
A-C-F	- 1.4		
F-D-A	+ 0.5		
A-C-F-D	- 0.9	112.3	-0.8
D-F-I	+ 0.5		
I-G-D	- 0.5		
D-F-I-G	0.0	113.1	0.0

continued....

Loops	Δh kJ/mol	$\sum \lvert \Delta h \rvert$ kJ/mol	Percent Deviation
A-B-H.	+41.1		
H-G-A	-39.8		
A-B-H-G	+ 1.3	142.9	+0.9
B-C-I	+42.2		
I-H-B	-43.9		
B-C-I-H	- 1.7	138.3	-1.2
A-C-I	+27.3		
I-G-A	-28.0		
A-C-I-G	- 0.7	169.2	-0.4

APPENDIX 3

FORMULAE AND SAMPLE CALCULATIONS

FORMULAE

A. Liquid Phase Analysis

1. Normality of Amine, N:

$$N = \frac{\text{ml of } H_2SO_4 \text{ used x normality of } H_2SO_4}{\text{ml of sample used}} \qquad (74)$$

2. Moles of CO_2 per mole of DEA, α_{CO_2}:

$$\alpha_{CO_2} = \frac{\left(\begin{matrix}\text{ml of HCl used to} \\ \text{titrate } BaCO_3 \text{ ppte.}\end{matrix}\right) \text{x normality of HCl}}{2 \text{ x } N \text{ x ml of sample used}} \qquad (75)$$

3. Moles of H_2S per mole of DEA, α_{H_2S}:

$$\alpha_{H_2S} = \frac{\left(\begin{matrix}\text{ml of } I_2 \text{ used x} \\ \text{Normality of } I_2\end{matrix}\right) - \left(\begin{matrix}\text{ml of } S_2O_3^- \text{ x} \\ \text{Normality of } S_2O_3^-\end{matrix}\right)}{2 \text{ x } N \text{ x ml of sample used}} \qquad (76)$$

B. Electric Energy from Heater

$$Q = IVt \qquad (77)$$

Units: joule = (ampere)(volt)(second)

where

$$I = \frac{\text{Voltage Drop Across 0.1 ohm Standard Resistor}}{0.1 \text{ ohm}}$$

V = Voltage Drop Across Heater

t = time clocked by timer

Since the voltage drops across the 0.1 ohm resistor and the heater were measured every 30 seconds, the quantity

IVt was computed as follows. The product IVt was calculated every 30 seconds (with t=30). This was repeated until the total time t was obtained. (Note the last interval may be for a time of less than 30 seconds.) The values of IVt were then summed to give Q, the total energy supplied to the system by means of the calorimeter heater.

C. Heat Capacity

$$Cp = \frac{Q}{m\ \Delta T} \qquad (78)$$

$$kJ/kg\ ^\circ C = \frac{kJ}{kg^\circ C}$$

SAMPLE CALCULATION

The sample calculation will be done for CO_2 in a 3.5 N DEA solution at 25°C, data set 2. The sample calculation is presented in two sections. Section A shows the calculations necessary to generate values for heat capacities and the differential heat of solution. Section B illustrates the calculations necessary to produce an enthalpy - concentration chart.

A. Heat Capacity and Heat of Solution

1st Step

RUN 156 - Electrical Run, Fresh 3.5 N DEA at 25°C.

α=0.000
Mass (of solution)=1036.4440g
Moles DEA=3.500

Q=13,227.4J From Eq. (77)
ΔT=33.43 mV=3.459°C From Eq.(70)
Cp=3.690 kJ/kg°C From Eq. (78)

Mass of Sample Removed after RUN 156=10.4182g
(for Analysis and Density Measurement)

RUN 157 - Electrical Run, Duplicate to Check Reproducibility of Cp.

α=0.000
Mass=1036.4440-Sample Removed
=1036.4440-12.5455=1023.8985g

Moles DEA=3.5 x $\frac{1023.8985}{1036.4440}$ = 3.458

Prorated for Moles of DEA removed in Sample taken after RUN 156.

Q=12,663.2J
ΔT=32.32 mV=3.344°C
Cp=3.698 kJ/kg°C

RUN 158C - 1st Chemical Run

Start of Run	End of Run
α=0.000	ΔT=34.60 mV
Moles DEA=3.458	α=0.057 From Eq. (75)
Moles CO_2= α(Moles DEA)=0.000	Moles DEA=3.458
Mass=1023.8985g	Moles CO_2=0.057 x 3.458
	=0.197
	Mass CO_2= (Moles CO_2)(Molecular Wt. of CO_2)
	= (0.197)(44.01)
	= 8.6699g
	Total Mass=1023.8985 + 8.6699
	=1032.5684g

RUN 159 - Electrical Equivalent of RUN 158C

α=0.057
Mass=1032.5684g
Moles DEA=3.458

Q=13,697.7J
ΔT=35.15 mV=3.637°C
Cp=3.647 kJ/kg°C

Mass of Sample Removed After RUN 159 = 12.6005g

RUN 160 - Electrical Run, Duplicate to Check Cp.

α=0.057
Mass=1032.5684-12.6005=1019.9679g
Moles DEA= 3.458 x $\frac{1019.9679}{1032.5684}$ =3.416

Q=12,209.9J
ΔT=31.79 mV=3.289°C
Cp=3.640 kJ/kg°C

RUN 161C - 2nd Chemical Run

Start of Run

α=0.057
Moles DEA=3.416
Moles CO_2=0.197 x $\frac{1019.9679}{1032.5684}$ = 0.195

Prorated for CO_2 removed in sample

Mass=1019.9679g

End of Run

ΔT=35.00 mV
α=0.103
Moles DEA=3.416
Moles CO_2=0.103 x 3.416
=0.352
Moles CO_2 added in this Run =
0.352-0.195=0.157
=6.9095g
Mass=1019.9679 + 6.9095
=1026.8775g

RUN 162 - Electrical Equivalent of RUN 161C

α=0.103
Mass=1026.8775g
Moles DEA=3.416

Q=13,280.3J
ΔT=34.59 mV=3.579°C
Cp=3.613 kJ/kg°C

Mass of Sample Removed after RUN 162=12.7329g

RUN 163 - Electrical Run, Duplicate to Check Cp

α=0.103
Mass=1026.8775-12.7329
=1014.1446g

Q=12,016.0J
ΔT=31.61 mV=3.270°C
Cp=3.623 kJ/kg°C

Moles DEA=3.416 x $\frac{1014.1446}{1026.8775}$ = 3.374

RUN 164C - 3rd Chemical Run

Start of Run

α=0.103
Moles DEA=3.374
Moles CO_2=0.352 x $\frac{1014.1446}{1026.8775}$ = 0.348

Mass = 1014.1446 g

End of Run

ΔT=33.50 mV
α=0.159
Moles DEA=3.374
Moles CO_2=0.159 x 3.374
=0.536
Moles CO_2 added in this Run = 0.536-0.348 = 0.188
= 8.2739g
Mass=1014.1446+8.2739
=1022.4185g

RUN 165 - Electrical Equivalent of RUN 164C

From this point the calculations are the same. The calculations are repeated for all the runs made. These calculations yield heat capacities. The next step illustrates the calculation of the heat released in the chemical runs and finally the differential heat of solution.

The general formula used in calculating the heat released in a chemical run is:

$$Q_{chem} = Q_{elec} \times \frac{\Delta T_{chem}}{\Delta T_{elec}} \qquad (79)$$

where Q is in Joules and ΔT in millivolts.

2nd Step

RUN 158C - 1st Chemical Run

$$Q_{158C} = Q_{159} \times \frac{\Delta T_{158C}}{\Delta T_{159}} = 13,697.7 \times \frac{34.60}{35.15} = 13,483.4J$$

RUN 161C - 2nd Chemical Run

$$Q_{161C} = Q_{162} \times \frac{\Delta T_{161C}}{\Delta T_{162}} = 13,280.8 \times \frac{35.00}{34.59} = 13,437.7J$$

RUN 164C - 3rd Chemical Run

$$Q_{164C} = Q_{165} \times \frac{\Delta T_{164C}}{\Delta T_{165}} = 12,129.2 \times \frac{33.50}{32.18} = 12,626.7J$$

RUN 167C - 4th Chemical Run

$$Q_{167C} = Q_{168} \times \frac{\Delta T_{167C}}{\Delta T_{168}}$$

From here on the calculations are the same, and they are done for all the chemical runs. A table of the cumulative moles of CO_2 reacted and the cumulative heat released is then compiled.

RUN NO.	This Run Q, J	Cumulative Moles CO_2 n_{cum}	Cumulative Heat Released Q_{cum}, J
158C	13,483.4	0.197	13,483.4
161C	13.437.7	0.352	26,921.1
164C	12,626.7	0.536	39,547.8
.	.	.	.
.	.	.	.

Once this table is completed the method of slopes described in Chapter III is used to generate the heat of solution data.

The sample calculations shown for RUNS 156-165 are listed in the first 10 lines and lines 31 to 30 of Table X in Appendix 4.

B. Enthalpy - Concentration Diagram

1. Reference Temperature 25°C

At 25°C, h_1' and h_2' are both set to zero and $h_{\alpha i}$ is calculated from Equations (43), (44), (55) and (56), etc.

RUN 158C - α = 0.057

From Eq. (44) $h_{\alpha 1}$ (per mole DEA) $= \frac{-13,483.4 \times 10^{-3}}{3.458}$

$= -3.900$ kJ/mol-DEA

From Eq.(43) $h_{\alpha 1}$ (per kg-soln) $= \frac{-13,483.4 \times 10^{-3}}{1032.5694}$

$= -13.058$ kJ/kg-soln.

RUN 161C - $\alpha = 0.103$

From Eq.(56) $h_{\alpha 2}$ (per mole DEA) $= \frac{[-13,483.4-13,437.7-(12.6005)(13.058)]10^{-3}}{3.416}$

$= \frac{-26,756.6}{3.416} = -7.833$ kJ/mol-DEA

From Eq.(55) $h_{\alpha 2} = \frac{-26,756.6}{1026.8775} = -26.056$ kJ/kg-soln.
(per kg-soln)

RUN 164C - $\alpha = 0.159$

From Eq.(58) $h_{\alpha 3}$ (per mole DEA) $= \frac{[-26,756.6-12,626.7-(12.7329)(-26.056)]10^{-3}}{3.374}$

$= \frac{-39.051.5}{3.374} = -11.574$ kJ/mol-DEA

From Eq.(57) $h_{\alpha 3} = \frac{-39,051.5}{1022.4185} = -38.195$ kJ/kg-soln.
(per kg-soln)

$h_{\alpha i}$ per mole of DEA and per kg of soln. can be calculated in the same fashion for the remainder of the chemical runs. The values for $h_{\alpha i}$ calculated here are listed in lines 2 to 4 of Table XV in Appendix 4.

2. Temperatures, 50°C and 75°C.

At 50°C and 75°C h_1' and h_2' are not zero. The only difference in the calculation of $h_{\alpha i}$ (compared with the above calculations), is the inclusion of the h_1' and h_2'

terms in Equations (43), (44), (55), and (56) etc.

a) Evaluation of h_1' at 50°C and 75°C:

From reference (24) h_1' at 50°C (i.e. T_2) referenced to 25°C (i.e. T_1), is obtained from the following equation:

$$h_1' = B(T_2-T_1) + C(T_2^2-T_1^2) + D(T_2^3-T_1^3) \quad (80)$$

where

$-T_1$ and T_2 are in °R

$-h_1'$ is in Btu/lb_m-CO_2 and

$B = 0.1143$, $C = 0.101132 \times 10^{-3}$

and $D = -0.026494 \times 10^{-6}$

Therefore at 50°C

$$h_1' = 0.11443(662-617)+0.101132 \times 10^{-3} (662^2-617^2)$$

$$\frac{Btu}{lb_m\text{-}CO_2} \quad -0.026249 \times 10^{-6} (662^3-617^3)$$

$$= 9.5068 \frac{Btu}{lb_m} = 0.973 \frac{kJ}{mol\text{-}CO_2}$$

Similarly at 75°C, $h_1' = 1.966 \frac{kJ}{mol\text{-}CO_2}$

b) Evaluation of h_2' at 50°C and 75°C

As mentioned in Chapter III

$$h_2' = \int_{T_1}^{T_2} Cp \, dT \quad (81)$$

h_2' at 50°C and 75°C is obtained from graphical integration of the smoothed Cp data (Figure 14) at $\alpha = 0$, with T_2 equal to 50°C and 75°C respectively and T_1 equal to 25°C (the reference temperature).

From Figure 14

h_2' at 50°C = 93.281 kJ/kg-soln = 27.628 kJ/mol-DEA

and

h_2' at 75°C = 188.741 kJ/kg-soln = 53.926 kJ/mol-DEA

With these values of h_1' and h_2' at 50°C and 75°C, $h_{\alpha i}$ at 50°C and 75°C can be evaluated from Equations (43), (44), (55), and (56) etc., in the same manner as was done for 25°C. Plotting of $h_{\alpha i}$ at 25°C, 50°C and 75°C all versus α results in the enthalpy-concentration diagram shown in Figure 15.

APPENDIX 4

EXPERIMENTAL DATA

Note: "C" denotes a "Chemical" run.

1) Experimental Data for CO_2 in 2.0 N DEA at 25°C.

TABLE VII

EXPERIMENTAL DATA, CO_2- 2.0 N DEA AT 25°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
44	0.000	28.4	11,781.1	3.936
45	"	25.1	10,440.4	3.949
47C	0.063	18.75	7,742.6	---
48	"	19.5	8,052.3	3.903
49	"	23.05	9,450.7	3.919
50C	0.145	27.60	11,250.8	---
51	"	29.45	12,044.9	3.866
52	"	29.80	12,047.2	3.884
53C	0.220	26.75	10,778.1	---
54	"	27.80	11,201.2	3.844
55	"	29.10	11,546.3	3.833
56C	0.310	28.65	11,367.6	---
59	"	33.25	13,192.8	3.813
60	"	34.1	13,087.0	3.799
61C	0.390	27.95	10,640.2	---
62	"	27.15	10,335.6	3.765
63	"	29.90	11,243.1	3.781
64C	0.469	25.90	9,779.3	---
65	"	26.90	10,157.0	3.773
66	"	28.35	10,523.5	3.758
67C	0.498	26.75	9,929.5	---
68	"	27.28	9,705.3	3.743
69	"	27.65	10,118.9	3.747

TABLE VII

Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J	ρ g/ml
44	0.000	0.000	0	1.023
47C	0.063	0.126	7,742.6	1.028
50C	0.145	0.286	18,993.4	1.034
53C	0.220	0.430	29,771.5	1.039
56C	0.310	0.586	41,139.1	1.048
61C	0.390	0.721	51,779.3	1.055
64C	0.469	0.855	61,558.6	1.061
67C	0.498	0.896	71,488.1	1.064

2) Experimental Data for CO_2 in 5.0 N DEA AT 25°C.

TABLE VIII

EXPERIMENTAL DATA, CO_2 - 5.0 N DEA at 25°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
75	0.000	31.11	11,460.6	3.380
76	"	27.41	10,101.6	3.383
77C	0.039	29.70	10,784.3	---
78	"	29.32	10,646.3	3.305
79	"	25.65	9,274.3	3.334
80C	0.071	29.68	10,645.4	---
81	"	28.20	10,114.6	3.284
82	"	27.32	9,730.0	3.307
83C	0.097	28.50	10,163.1	---
84	"	27.61	9,845.7	3.287
85	"	28.36	9,975.1	3.283
86C	0.134	33.46	11,793.1	---
87	"	32.17	11,338.4	3.258
88	"	28.95	10,301.7	3.251

TABLE VIII - Continued

RUN No.	α	ΔT mV	Q J	Cp kJ/kg-°C
89C	0.166	29.68	10,180.4	---
90	"	27.06	9,281.8	3.198
91	"	27.28	9,234.8	3.196
92C	0.198	31.07	10,718.2	---
93	"	27.48	9,479.8	3.169
94	"	30.38	9,572.0	3.120
95C	0.227	30.93	10,376.7	---
96	"	27.67	9,283.0	3.171
97	"	27.53	9,194.6	3.198
98C	0.247	30.61	10,120.5	---
99	"	27.65	9,141.8	3.153
100	"	30.52	8,929.4	3.145
101C	0.289	34.53	11,301.1	---
102	"	29.59	9,684.3	3.136
103	"	26.28	8,491.5	3.139
104C	0.328	30.63	9,640.8	---
105	"	29.09	9,156.1	3.034
106	"	26.29	8,070.5	3.000
107C	0.373	29.53	9,294.8	---
108	"	26.31	8,281.3	3.086
109	"	25.73	8,079.3	3.085
110C	0.401	28.41	9,016.1	---
111	"	26.98	8,562.3	3.101
112	"	26.93	8,430.7	3.102
113C	0.419	28.46	8,931.9	---
114	"	26.85	8,426.6	3.099
115	"	26.19	8,157.9	3.120
116C	0.452	27.27	8,545.3	---
117	"	26.95	8,263.3	3.119
118	"	26.14	8,065.6	3.116
119C	0.496	27.54	8,449.1	---
120	"	26.42	8,105.5	3.072

TABLE VIII - Continued

RUN NO.	α	ΔT mV	Q J	kJ/kg°C
121	0.496	26.49	8,108.8	3.110
122C	0.555	27.78	8,541.8	---
123	"	26.59	8,175.9	3.090

RUN NO.	α	n_{cum} mol	Q_{cum} J	ρ g/ml
75	0.000	0.000	0	1.053
77C	0.039	0.194	10,784.3	1.066
80C	0.071	0.348	21,429.7	1.071
83C	0.097	0.471	31,592.8	1.077
86C	0.134	0.645	43,385.9	1.085
89C	0.166	0.790	53,566.3	1.094
92C	0.198	0.931	64,284.5	1.097
95C	0.227	1.051	74,661.2	1.105
98C	0.247	1.129	84,781.7	1.109
101C	0.289	1.306	96,082.8	1.117
104C	0.328	1.462	105,723.6	1.123
107C	0.373	1.640	115,018.4	1.133
110C	0.401	1.740	124,034.5	1.136
113C	0.419	1.791	132,966.4	1.143
116C	0.452	1.905	141,511.7	1.148
119C	0.496	2.059	149,960.8	1.150
122C	0.555	2.270	158,502.6	1.160

3) Experimental Data for CO_2 in 3.5 N DEA AT 25°C.

TABLE IX

EXPERIMENTAL DATA, CO_2 - 3.5 N DEA AT 25°C, SET 1

RUN No.	α	ΔT mV	Q J	Cp kJ/kg.°C
124	0.000	27.49	10,882.6	3.690
125	"	27.72	10,826.0	3.685

TABLE IX - Continued

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg.°C
126	0.000	27.75	10,879.4	3.698
127C	0.047	29.21	11,387.8	---
128	"	28.59	11,146.1	3.651
129	"	37.66	14,568.1	3.662
130C	0.091	30.63	11,677.2	---
131	"	28.94	11,032.9	3.589
132	""	29.20	11,124.0	3.631
133C	0.149	32.28	12,262.4	---
134	"	32.75	12,440.9	3.589
135	"	30.59	11,428.3	3.574
136C	0.205	34.78	12,976.1	---
137	"	34.18	12,752.3	3.540
138	"	32.14	11,886.9	3.555
139C	0.254	34.88	12,859.3	---
140	"	32.13	11,845.5	3.519
141	"	31.35	11,381.0	3.510
142C	0.316	34.26	12,390.5	---
143	"	31.69	11,461.0	3.466
144	"	31.69	11,424.5	3.500
145C	0.375	35.08	12,687.1	---
146	"	32.36	11,703.4	3.482
147	"	31.52	11,219.6	3.473
148C	0.433	35.55	12,691.1	---
149	"	31.65	11,298.8	3.455
150	"	31.92	11,223.4	3.449
151	0.487	31.27	10,535.2	---
152	"	32.81	10,788.4	3.201
153	"	31.85	10,408.3	3.225
154	0.559	31.07	10,153.4	---
155	"	31.35	10,115.9	3.153

TABLE IX - Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J	ρ g/ml
124	0.000	0.000	0	1.039
127C	0.047	0.164	11,387.8	1.048
130C	0.091	0.310	23,065.0	1.056
133C	0.149	0.504	35,327.4	1.060
136C	0.205	0.683	48,303.5	1.067
139C	0.254	0.836	61,162.8	1.079
142C	0.316	1.028	73,553.3	1.086
145C	0.375	1.202	86,240.4	1.092
148C	0.433	1.370	98,931.5	1.104
151C	0.450	1.522	109,466.7	1.111
154C	0.512	1.723	119,620.1	1.119

TABLE X

EXPERIMENTAL DATA, CO_2 - 3.5 N DEA AT 25°C, SET 2

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
156	0.000	33.43	13,227.4	3.690
157	"	32.32	12,663.2	3.698
158C	0.057	34.60	13,483.4	---
159	"	35.15	13,697.7	3.647
160	"	31.79	12,209.9	3.640
161C	0.103	35.00	13,437.7	---
162	"	34.59	13,280.3	3.613
163	"	31.61	12,016.0	3.623
164C	0.159	33.50	12,626.7	---

TABLE X - Continued

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg.-°C
165	0.159	32.18	12,129.2	3.564
166	"	31.31	11,691.6	3.575
167C	0.211	34.10	12,655.5	---
168	"	33.20	12,321.5	3.543
169	"	32.25	11,904.8	3.554
170C	0.263	34.10	12,519.5	---
171	"	32.26	11,844.0	3.507
172	"	31.63	11,496.5	3.517
173C	0.341	49.77	18,149.6	---
174	"	44.73	16,311.7	3.487
175	"	31.98	11,481.2	3.481
176C	0.391	34.03	12,278.1	---
177	"	31.22	11,264.3	3.474
178	"	31.92	11,325.0	3.461
179C	0.450	31.19	11,143.5	---
180	"	32.03	11,443.6	3.457
181	"	31.61	11,127.4	3.453
182C	0.512	31.09	10,995.4	---
183	"	31.85	11,264.2	3.439
184	"	32.50	11,235.4	3.408

TABLE X - Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J	ρ g/ml
156	0.000	0.000	0	1.042
158C	0.057	0.197	13,483.4	1.050
161C	0.103	0.352	26,921.1	1.056
164C	0.159	0.536	39,547.8	1.066
167C	0.211	0.701	52,203.3	1.072
170C	0.263	0.864	64,722.8	1.081
173C	0.341	1.108	82,872.4	1.092
176C	0.391	1.253	95,150.5	1.100
179C	0.450	1.422	106,294.0	1.107
182C	0.512	1.596	117,289.4	1.113

4) Experimental Data CO_2 in 3.5 N DEA AT 50°C

TABLE XI

EXPERIMENTAL DATA, CO_2 - 3.5 N DEA AT 50°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
195	0.000	31.42	16,094.1	3.766
196	0.000	31.32	16,071.4	3.772
197C	0.056	32.67	16,464.9	---
198	"	32.18	16,218.0	3.717
199C	0.122	32.31	16,165.0	---
200	"	32.70	16,360.1	3.697
201C	0.188	33.38	16,538.9	---
202	"	33.25	16,474.5	3.670
203C	0.254	32.68	15,681.9	---
204	"	32.34	15,518.7	3.620
205C	0.326	32.45	15,651.4	---
206	"	31.62	15,251.1	3.600
207C	0.402	32.09	15,290.5	---
208	"	31.33	14,928.3	3.565
209C	0.596	28.92	13,624.1	---

TABLE XI - Continued

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
210	0.596	29.62	13,953.9	3.484
211C	0.726	27.25	12,582.4	---
212	"	28.08	12,965.6	3.406
213	"	34.24	15,639.2	3.391

TABLE XI - Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J
197C	0.056	0.194	16,464.9
199C	0.122	0.415	32,629.9
201C	0.188	0.636	49,168.8
203C	0.254	0.844	64,850.7
205C	0.326	1.073	80,502.1
207C	0.402	1.304	95,792.6
209C	0.596	1.908	109,416.7
211C	0.726	2.294	121,999.1

5) Experimental Data CO_2 in 2.0 N DEA AT 50°C

TABLE XII

EXPERIMENTAL DATA CO_2 - 2.0 N DEA AT 50°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
214	0.000	27.17	14,071.4	3.900
215	"	30.01	15,489.5	3.872
216C	0.087	27.93	14,180.8	---
217	"	28.78	14,612.4	3.833
218C	0.193	27.72	13,871.7	---
219	"	27.30	13,661.6	3.797
220C	0.299	27.48	13,580.3	---
221	"	27.05	13,367.8	3.765
222C	0.417	27.46	13,416.9	---

TABLE XII - Continued

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
223	0.417	25.74	12,576.5	3.741
224C	0.591	23.15	11,151.3	---
225	"	23.08	11,117.6	3.699
226C	0.690	21.18	9,941.3	---
227	"	21.51	10,096.2	3.634
228	"	26.32	12,289.2	3.631

TABLE XII - Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J
216C	0.087	0.172	14,180.8
218C	0.193	0.376	28,052.5
220C	0.299	0.576	41,632.8
222C	0.417	0.793	55,049.7
224C	0.591	1.110	66,201.0
226C	0.690	1.278	76,142.3

6) Experimental Data for CO_2 in 3.5 N DEA AT 75°C

TABLE XIII

EXPERIMENTAL DATA CO_2 - 3.5 N DEA AT 75°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
234	0.000	13.50	12,701.1	3.923
235	"	13.54	12,717.2	3.916
236C	0.043	13.57	12,572.1	---
237	"	13.77	12,757.3	3.836
238C	0.087	14.59	13,477.4	---
239	"	14.48	13,375.7	3.839
240C	0.128	14.16	12,966.8	---
241	"	14.05	12,866.1	3.824
242C	0.181	14.01	12,605.2	---

TABLE XIII - Continued

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
243	0.181	14.15	12,731.2	3.783
244C	0.232	14.08	12,607.1	---
245	"	13.79	12,347.5	3.788
246C	0.294	13.93	12,369.2	---
247	"	13.45	11,943.0	3.775
248C	0.354	14.00	12,179.4	---
249	"	13.71	11,927.1	3.745
250C	0.427	13.78	11,538.4	---
251	"	13.86	11,605.4	3.722

TABLE XIII - Continued

RUN NO.	α	n_{cum} mol	Q_{cum} J
236C	0.043	0.149	12,572.1
238C	0.087	0.299	26,049.5
240C	0.128	0.438	39,016.3
242C	0.181	0.610	51,621.5
244C	0.232	0.773	64,228.6
246C	0.294	0.966	76,597.8
248C	0.354	1.150	88,777.2
250C	0.427	1.368	100,315.6

7) Smoothed Heat Capacity Data

TABLE XIV

SMOOTHED HEAT CAPACITY DATA, CO_2 - 3.5 N DEA SYSTEM AT 25°C, 50°C AND 75°C RESPECTIVELY

α	kJ/kg -°C TEMPERATURE °C		
	25	50	75
0.0	3.694	3.770	3.904
0.1	3.607	3.703	3.828
0.2	3.552	3.653	3.795
0.3	3.502	3.610	3.765
0.4	3.466	3.568	3.728
0.5	3.433	3.530	3.665
0.6	---	3.480	---
0.7	---	3.420	---

8) Data for Enthalpy - Concentration Diagram

TABLE XV

$h_{\alpha i}$, CO_2 - 3.5 N DEA SYSTEM AT 25°C

RUN NO.	α	h kJ/mol DEA	h kJ/kg soln.
157	0.000	0	0
158C	0.057	-3.900	-13.058
161C	0.103	-7.833	-26.056
164C	0.159	-11.574	-38.195
167C	0.211	-15.376	-50.350
170C	0.263	-19.182	-62.345
173C	0.341	-24.773	-79.619
176C	0.391	-28.604	-91.292
179C	0.450	-32.128	-101.700
182C	0.512	-35.652	-111.888

TABLE XVI

$h_{\alpha i}$, CO_2 - 3.5 N DEA SYSTEM AT 50°C

RUN NO.	α	h kJ/mol DEA	h kJ/kg soln.
196	0.000	27.628	93.281
197C	0.056	22.921	76.747
199C	0.122	18.251	60.528
201C	0.188	13.412	44.051
203C	0.254	8.767	28.525
205C	0.326	4.077	13.128
207C	0.402	-0.561	-1.788
209C	0.596	-4.626	-14.349
211C	0.726	-8.479	-25.842

TABLE XVII

$h_{\alpha i}$, CO_2 - 3.5 N DEA SYSTEM AT 75°C

RUN NO.	α	h kJ/mol DEA	h kJ/kg soln.
235	0.000	53.926	182.180
236C	0.043	50.418	169.254
238C	0.087	46.607	155.451
240C	0.128	42.894	142.196
242C	0.181	39.261	129.165
244C	0.232	35.579	116.185
246C	0.294	31.936	103.373
248C	0.354	28.304	90.833
250C	0.427	24.847	78.927

9) Experimental Data H_2S in 3.5 N DEA AT 25°C

TABLE XVIII

EXPERIMENTAL DATA, H_2S - 3.5 N DEA AT 25°C

RUN NO.	α	ΔT mV	Q J	Cp kJ/kg-°C
259	0.000	26.17	10,368.8	3.691
260	"	29.12	11,599.1	3.709
261C	0.082	28.60	11,302.4	---
262	"	28.55	11,282.6	3.646
263C	0.164	30.55	11,892.5	---
264	"	31.78	12,371.4	3.599
265C	0.246	30.10	11,557.2	---
266	"	32.64	12,532.5	3.561
267C	0.332	30.41	11,473.3	---
268	"	31.02	11,703.4	3.509
269C	0.412	30.17	11,257.3	---
270	"	30.64	11,432.7	3.485
271C	0.493	29.93	11,041.1	---
272	"	30.64	11,303.0	3.456
273C	0.575	32.33	11,797.1	---
274	"	31.02	11,319.1	3.430
275C	0.662	33.68	12,185.5	---
276	"	31.03	11,226.7	3.413
277C	0.744	31.80	11,372.7	---
278	"	30.59	10,940.0	3.390
279C	0.836	33.09	11,718.6	---
280	"	31.58	11,183.8	3.370
281C	0.901	31.23	10,927.9	---
282	"	31.77	11,116.9	3.356

TABLE XVIII - Continued

RUN NO.	α	h_{cum} mol	Q_{cum} J
261C	0.082	0.288	11,302.4
263C	0.164	0.569	23,194.9
265C	0.246	0.839	34,752.1
267C	0.332	1.119	46,225.4
269C	0.412	1.371	57,482.1
271C	0.493	1.623	68,523.8
273C	0.575	1.871	80,320.9
275C	0.662	2.125	92,506.4
277C	0.744	2.355	103,879.1
279C	0.836	2.611	115,597.7
281C	0.901	2.774	126,525.6